

11/02/00

JC949 U.S. PTO

UTILITY PATENT APPLICATION TRANSMITTAL

Only for new nonprovisional applications under 37 CFR 1.53(b))

Attorney Docket No.

09792909-4689

First Named Inventor or Application Identifier

Tetsuo Shibamura

Express Mail Label No: EL654782474US

JC920 U.S. PTO
09/704968

11/02/00

ADDRESS TO: Assistant Commissioner for Patents
Box Patent Application
Washington, DC 20231

APPLICATION ELEMENTS

See MPEP chapter 600 concerning utility patent application contents.

ACCOMPANYING APPLICATION PARTS

1. ☒ Specification Total Pages 95
2. ☒ Drawing(s) (35USC 113) Total Pages 7
3. ☒ Declaration and Power of Attorney Total Pages 5
- a. ☒ Unexecuted(original or copy)
- b. ☐ Copy from prior application (37CFR 1.63(d))
(for continuation/divisional with Box 14 completed)
- [Note Box 4 Below]
- i. ☐ **DELETION OF INVENTOR(S)**
Signed statement attached deleting Inventor(s) named in the prior application, see 37 CFR 1.63(d)(2) and 1.33(b).
- ☐ Incorporation By Reference (usable if Box 3b is checked)
The entire disclosure of the prior application, from which copy of the oath or declaration is supplied under Box 3b, is considered as being part of the disclosure of the accompanying application and is hereby incorporated by reference therein.

5. ☐ Assignment Papers (cover sheet & documentation)
6. ☒ Letter under 37 CFR 1.41(c).
7. ☐ English Translation Document (if applicable)
8. ☐ Information Disclosure Statement (IDS)/PTO-1449 ☐ Copies of IDS Citations
9. ☒ Preliminary Amendment
10. ☒ Return Receipt Postcard (MPEP 503)
(Should be specifically itemized)
11. ☐ Small Entity ☐ Statement filed in prior Application, Statement(s) Status still proper and desired
12. ☒ Certified copy of Japanese priority applications Nos. P11-312071 filed November 2, 1999

14. If a CONTINUING APPLICATION, check appropriate box and supply the requisite information:

☐ Continuation ☐ Divisional ☐ Continuation-in-part (CIP) ☐ of prior application No:

CLAIMS AS FILED

	(1) FOR	(2) NUMBER FILED	(3) NUMBER EXTRA	(4) RATE	(5) BASIC FEE \$710.00
TOTAL CLAIMS	20	10		18.00	0.00
INDEPENDENT CLAIMS	03	4	1	80.00	80.00
ANY MULTIPLE DEPENDENT CLAIMS? <input type="checkbox"/> YES <input checked="" type="checkbox"/> NO					0.00
TOTAL FEE					\$790.00

☒ The Commissioner is hereby authorized to charge the filing fee of \$373.00 and any additional fees which may be required in connection with this application, or credit any overpayment to ACCOUNT NO. 19-3140. A duplicate copy of this sheet is enclosed.

☒ A check in the amount of \$790.00 to cover the filing fee is enclosed.

15. CORRESPONDENCE ADDRESS: David R. Metzger
SONNENSCHN NATH & ROSENTHAL
P.O. Box #061080
Wacker Drive Station, Sears Tower
Chicago, IL 60606-1080
Customer ID #26263
Telephone (312) 876-8000 - Fax (312) 876-7934

SIGNATURE

David R. Metzger (Reg. No. 32919)

Date: November 2, 2000

U-11

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

PRELIMINARY AMENDMENT ACCOMPANYING APPLICATION

APPLICANT: Tetsuo Shibamura, et al. ATTY. DOCKET NO. 09792909-4689

SERIAL NO.

DATE FILED:

INVENTION: "BATHOPHENATHROLINE COMPOUND AND PROCESS FOR
PREPARING SAME"

Assistant Commissioner of Patents
Washington, D.C. 20231

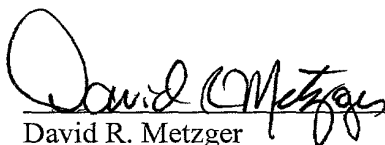
S I R:

Between the title and the heading "Background of the Invention" on page 1, insert the
following:

--RELATED APPLICATION DATA

The present application claims priority to Japanese Application No. P11-312071 filed
November 2, 1999, which application is incorporated herein by reference to the extent
permitted by law.

Respectfully submitted,

 (Reg. No. 32,919)
David R. Metzger

SONNENSCHN NATH & ROSENTHAL
P.O. Box #061080
Wacker Drive Station
Sears Tower
Chicago, IL 60606-1080
Customer #26263

Attorneys for Applicant(s)

09792909-4689

500P:325**00

BATHOPHENANTHROLINE COMPOUND AND
PROCESS FOR PREPARING SAME

BACKGROUND OF THE INVENTION

This invention relates to a bathophenanthroline compound, which is adapted for use in an organic electroluminescent device (e.g. an organic electroluminescent device suitable as a display device or a light-emitting device such as a spontaneous light flat display, especially an organic electroluminescent color display using an organic thin film as an electroluminescent layer), and also a process for preparing the compound.

In recent years, importance of interfaces between human beings and machines including multimedia-oriented commercial articles is exalted. For more comfortable and more efficient machine operations, it is necessary to retrieve information from an operated machine without failure simply, instantaneously and in an adequate amount. To this end, studies have been made on various types of display devices or displays.

As machines are now miniaturized, there is an increasing demand, day by day, for miniaturization and thinning of display devices. For instance, there is an

09704968-140200

inconceivable development with respect to the miniaturization of lap top-type information processors of the all-in-one type such as notebook-size personal computers, notebook-size word processors and the like. This, in turn, entails a remarkable technical innovation on liquid crystal displays for use as a display device for the processor.

Nowadays, liquid crystal displays are employed as an interface of a diversity of articles and have wide utility in the fields not only of lap top-type information processors, but also of articles for our daily use including small-sized television sets, watches, desk-top calculators and the like.

These liquid crystal displays have been studied as a key of display devices, which are used as the interface connecting a human being and a machine and cover small-sized to large capacitance display devices while making use of the feature that liquid crystals are low in drive voltage and power consumption. However, liquid crystal displays have the problems that they do not rely on spontaneous light and thus need a greater power consumption for back light drive than for liquid crystal drive, with the result that a service time is shortened when using a built-in battery, thus placing a limitation

on their use. Moreover, the liquid crystal display has another problem that it has such a narrow angle of field as not to be suitable for use as a large-sized display device.

Furthermore, the liquid crystal display depends on the manner of display using the orientation of liquid crystal molecules, and this is considered to bring about a serious problem that its contrast changes depending on the angle even within an angle of field.

From the standpoint of drive systems, an active matrix system, which is one of drive systems, has a response speed sufficient to deal with a motion picture. However, since a TFT (thin film transistor) drive circuit is used, a difficulty is involved in making a large screen size owing to the pixel defects, thus being disadvantageous in view of the reduction in cost.

In the liquid crystal display, a simple matrix system, which is another type of drive system, is not only low in cost, but also relatively easy in making a large screen size. However, this system has the problem that its response speed is not enough to deal with a motion picture.

In contrast, a spontaneous light display device is now under study such as on a plasma display device, an

inorganic electroluminescent device, an organic electroluminescent device and the like.

The plasma display device employs plasma emission in a low pressure gas for display and is suited for the purposes of a large size and large capacitance, but has the problem on thinning and costs. In addition, an AC bias of high potential is required for its drive, and thus, the display is not suitable as a portable device.

The inorganic electroluminescent device has been put on the market as a green light emission display. Like the plasma display device, an AC bias drive is essential, for which several hundreds of volts are necessary, thus not being of practical use.

In this connection, however, emission of three primaries including red (R), green (G) and blue (B) necessary for color display has been succeeded due to the technical development. Since inorganic materials are used for this purpose, it has been difficult to control emission wavelengths depending on the molecular design or the like. Thus, it is believed that full color display is difficult.

On the other hand, the electroluminescent phenomenon caused by organic compounds has been long studied ever since there was discovered a luminescent or

09704968.110200

emission phenomenon wherein carriers are injected into the single crystal of anthracene capable of emitting a strong fluorescence in the first part of 1960s. However, such fluorescence is low in brightness and monochronous in nature, and the single crystal is used, so that this emission has been made as a fundamental investigation of carrier injection into organic materials.

However, since Tang et al. of Eastman Kodak have made public an organic thin film electroluminescent device of a built-up structure having an amorphous luminescent or emission layer capable of realizing low voltage drive and high brightness emission in 1987, extensive studies have been made, in various fields, on the emission, stability, rise in brightness, built-up structure, manner of fabrication and the like with respect to the three primaries of R, G and B.

Furthermore, diverse novel materials have been prepared with the aid of the molecular design inherent to an organic material. At present, it starts to conduct extensive studies on applications, to color displays, of organic electroluminescent devices having excellent characteristic features of DC low voltage drive, thinning, and spontaneous light emission and the like.

The organic electroluminescent device (which may be

002017 88640260

sometimes referred to as organic EL device hereinafter) has a film thickness of 1 μm or below. When an electric current is charged to the device, the electric energy is converted to a light energy thereby causing luminescence to be emitted in the form of a plane. Thus, the device has an ideal feature for use as a display device of the spontaneous emission type.

Fig. 7 shows an example of a known organic EL device. An organic EL device 10 includes, on a transparent substrate 6 (e.g. a glass substrate), an ITO (indium tin oxide) transparent electrode 5, a hole transport layer 4, an emission layer 3, an electron transport layer 2, and a cathode 1 (e.g. an aluminium electrode) formed in this order, for example, by a vacuum deposition method.

A DC voltage 7 is selectively applied between the transparent electrode 5 serving as an anode and the cathode 1, so that holes serving as carriers charged from the transparent electrode 5 are moved via the hole transport layer 4, and electrons charged from the cathode 1 are moved via the electron transport layer 2, thereby causing the re-combination of the electrons-holes. From the site of the re-combination, light 8 with a given wavelength is emitted and can be observed from the side

of the transparent substrate 6.

The emission layer 3 may be made of a light-emitting substance such as, for example, anthracene, naphthalene, phenanthrene, pyrene, chrysene, perylene, butadiene, coumarin, acridine, stilbene and the like. This may be contained in the electron transport layer 2.

Fig. 8 shows another example of an organic EL device. In an organic EL device 20, the emission layer 3 as in Fig. 7 is omitted and, instead, such a light-emitting substance as mentioned above is contained in the electron transport layer 2, and thus, the organic EL device 20 is so arranged as to emit light 18 having a given wavelength from an interface between the electron transport layer 2 and the hole transport layer 4.

Fig. 9 shows an application of the organic EL device. More particularly, a built-up body of the respective organic layers (including the hole transport layer 4, and the emission layer 3 or the electron transport layer 2) is interposed between the cathode 1 and the anode 5. These electrodes are, respectively, provided in the form of stripes that are intersected in the form of a matrix. In this state, a signal voltage is applied to in time series by means of a luminance signal circuit 34 and a shift register-built in control circuit

35 so that light is emitted at a number of intersected points (pixels), respectively.

Such an arrangement as set out above is usable not only as a display, but also as an image reproducing apparatus. It will be noted that if the striped pattern is provided for the respective colors of R, G and B, there can be obtained a full color or a multi-color arrangement.

In a display device made of a plurality of pixels using the organic EL device, emitting organic thin film layers 2, 3 and 4 are usually sandwiched between the transparent electrode 5 and the metal electrode 1, and emission occurs at the side of the transparent electrode 5.

For use as constituting materials of the organic EL device, attention has now been drawn to organic luminescent materials and carrier transport materials suitable for use in combination with the organic luminescent materials. The advantages of these organic materials reside in that their optical and electrical properties can be controlled to some extent through the molecular design thereof. When an organic luminescent material having a given light emission and a carrier transport material suited therewith are used in

combination, efficient light emission is ensured.

Accordingly, there can be realized a full color organic EL device wherein primaries of R, G and B are emitted using the respective luminescent materials.

In some case, such an organic EL device as set out above may have such a structure that a hole transport layer serves also as a luminescent element. In this device structure, it is essential to provide a carrier transport layer that is able to efficiently transport electrons and block holes. However, organic materials that satisfy the above requirement and the efficient manufacture of these materials have never been found yet.

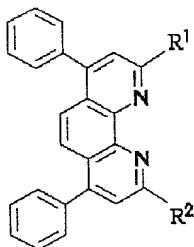
SUMMARY OF THE INVENTION

An object of the invention is to provide a novel organic material, which is suitable for use as a carrier transport material capable of efficiently transporting electrons and blocking holes.

Another object of the invention is to provide a process for preparing such an organic compound as mentioned above in an efficient manner.

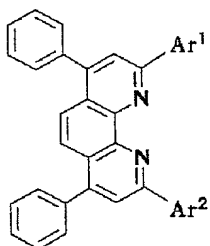
According to an aspect of the invention, there is provided a bathophenanthroline compound of the following general formula [I] or [II]

General Formula [I]:



wherein R¹ and R² may be the same or different and independently represent a linear, branched or cyclic, saturated or unsaturated hydrocarbon group, or a substituted or unsubstituted, saturated or unsaturated hydrocarbon group provided that at least one of R¹ and R² has at least two carbon atoms, or

General Formula [II]:



wherein Ar¹ and Ar² may be the same or different and independently represent a substituted or unsubstituted aryl group.

The bathophenanthroline compound of the invention

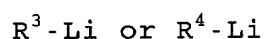
002017-88640250

can control carrier transportability depending on the type of substituent introduced into the molecule, and can thus be utilizable as a carrier transport material of various types of organic EL devices. The compounds have high glass transition point and high melting point and are stable electrically, thermally and/or chemically. In addition, the compounds are sublimable in nature, which is advantageous in that a uniform amorphous film can be readily formed according to a vacuum deposition process.

In the bathophenanthroline compounds of the formulas [I] and [II], it is preferred that R^1 and R^2 , and Ar^1 and Ar^2 are, respectively, the same. It will be noted that the term "aryl group" used herein means a carbocyclic aromatic group such as, for example, a phenyl group, a naphthyl group, an anthryl group or the like, and a heterocyclic aromatic group such as, for example, a furyl group, a thienyl group, a pyridyl group or the like.

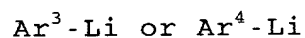
According to another aspect of the invention, there is also provided a process for preparing a bathophenanthroline compound, which comprising subjecting a lithium compound of the following general formula [III] or [V]

General Formula [III]:



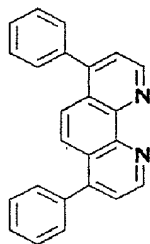
wherein R^3 and R^4 may be the same or different and independently represent a linear, branched or cyclic, saturated or unsaturated hydrocarbon group or a substituted or unsubstituted, saturated or unsaturated hydrocarbon group provided that at least one of R^3 and R^4 has at least two carbon atoms, or

General Formula [V]:



wherein Ar^3 and Ar^4 may be the same or different and independently represent a substituted or unsubstituted aryl group, and bathophenanthroline of the following formula [IV]

Structural Formula [IV]:



to nucleophilic substitution reaction to obtain a bathophenanthroline compound of the afore-indicated formula [I] or [II].

According to the preparation process of the invention, the bathophenanthroline compound of the

invention can be efficiently prepared. It is preferred that in the course of the nucleophilic substitution reaction, carbanions are generated from the lithium compound and subsequently reacted with the bathophenanthroline.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic sectional view showing an essential part of an organic EL device using a bathophenanthroline compound of the invention;

Fig. 2 is a schematic band model view showing a built-up structure of the organic EL device;

Fig. 3 is schematic sectional view showing a vacuum deposition apparatus used to make the organic EL device;

Fig. 4 is a plan view showing the organic EL device;

Fig. 5 is a schematic sectional view showing an essential part of another type of organic EL device using a bathophenanthroline compound of the invention;

Fig. 6 is a schematic sectional view showing an essential part of further another type of organic EL device using a bathophenanthroline compound of the invention;

Fig. 7 is a schematic sectional view showing an

example of a prior-art organic EL device;

Fig. 8 is a schematic sectional view showing an example of another type of prior-art organic EL device; and

Fig. 9 is a schematic perspective view showing an example of further another type of prior-art organic EL device.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The bathophenanthroline compound of the invention is described in more detail. In the compound of the general formula [I], R^1 and R^2 independently represent a linear, branched or cyclic, saturated or unsaturated hydrocarbon group. Specific examples include an ethyl group, a butyl group, an n-propyl group, an isopropyl group, an n-butyl group, a sec-butyl group, a tert-butyl group, an n-pentyl group, an iso-pentyl group, a neopentyl group, a tert-pentyl group, a cyclopentyl group, an n-hexyl group, a 2-ethylbutyl group, a 3,3-dimethylbutyl group, a cyclohexyl group, an n-heptyl group, a cyclohexylmethyl group, an n-octyl group, a tert-octyl group, a 2-ethylhexyl group, an n-nonyl group, an n-decyl group, an n-dodecyl group, an n-tetradecyl group, an n-hexadecyl group and the like although not

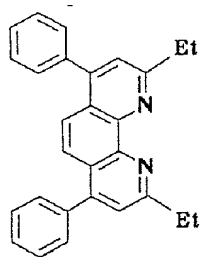
limited to those mentioned above.

Specific examples of the substituted or unsubstituted, saturated and unsaturated hydrocarbon group for R^1 and R^2 include a benzyl group, a phenethyl group, an α -methylbenzyl group, an α,α -dimethylbenzyl group, a 1-naphthylmethyl group, a 2-naphthylmethyl group, a furfuryl group, a 2-methylbenzyl group, a 3-methylbenzyl group, a 4-methylbenzyl group, a 4-ethylbenzyl group, a 4-isopropylbenzyl group, a 4-tert-butylbenzyl group, a 4-n-hexylbenzyl group, a 4-nonylbenzyl group, a 3,4-dimethylbenzyl group, and the like saturated or unsaturated hydrocarbon group although not limited to those mentioned above.

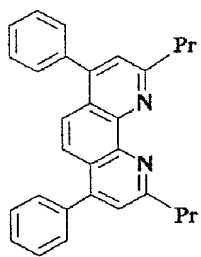
In the general formula [II], Ar^1 and Ar^2 independently represent a substituted or unsubstituted aryl group. Specific examples include a phenyl group, a 1-naphthyl group, a 2-anthryl group, a 9-anthryl group, a 2-fluorenyl group, a 4-quinolyl group, a pyridyl group, a 3-pyridynyl group, a 2-pyridynyl group, a 3-furyl group, a 2-furyl group, a 3-thienyl group, a 2-oxazolyl group, a 2-thiazolyl group, a 2-benzoxazolyl group, a 2-benzothiazolyl group, a 2-benzimidazolyl group, a 4-methylphenyl group, a 3-methylphenyl group, a 2-methylphenyl group, a 2,3-dimethylphenyl group, a 2,4-

dimethylphenyl group, a 2,5-dimethylphenyl group, a 2,6-dimethylphenyl group, a 3,4-dimethylphenyl group, a 3,5-dimethylphenyl group, a 2,3,4-trimethylphenyl group, a 2,3,5-trimethylphenyl group, a 2,3,6-trimethylphenyl group, a 3,4,5-trimethylphenyl group, a 4-ethylphenyl group, a 3-ethylphenyl group, a 2-ethylphenyl group, a 2,3-diethylphenyl group, a 2,4-diethylphenyl group, a 2,5-diethylphenyl group, a 2,6-diethylphenyl group, a 3,4-diethylphenyl group, a 3,5-diethylphenyl group, a 2,3,4-triethylphenyl group, a 2,3,5-triethylphenyl group, a 2,3,6-triethylphenyl group, a 3,4,5-triethylphenyl group, a 4-n-propylphenyl group, a 4-isopropylphenyl group, a 2-isopropylphenyl group, a 4-n-butylphenyl group, a 4-isobutylphenyl group, a 4-sec-butylphenyl group, a 4-tert-butylphenyl group, a 3-tert-butylphenyl group, a 2-tert-butylphenyl group and the like although not limited to those mentioned above.

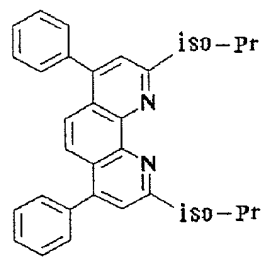
Specific examples of the bathophenanthroline compound of the invention includes those mentioned below as Compound Nos. 1 to 178, but these compounds should not be construed as limitation thereof. In the specific compounds, Me represents a methyl group, Et represents an ethyl group, Pr represents a propyl group, and Bu represents a butyl group.



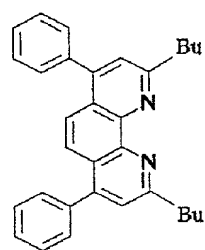
Compound No. 1



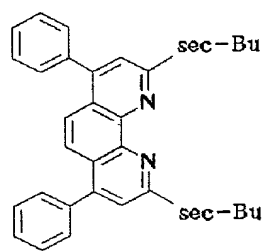
Compound No. 2



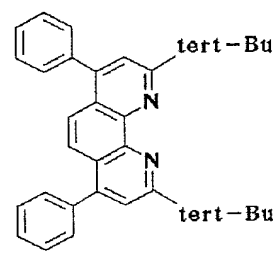
Compound No. 3



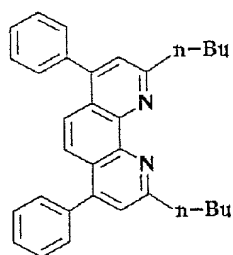
Compound No. 4



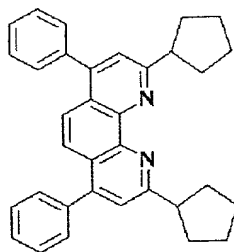
Compound No. 5



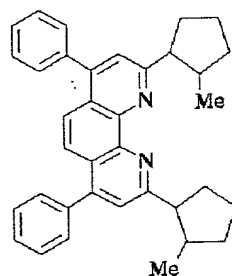
Compound No. 6



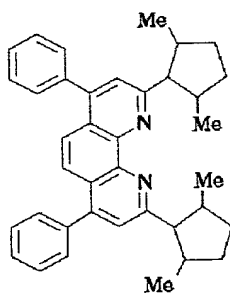
Compound No. 7



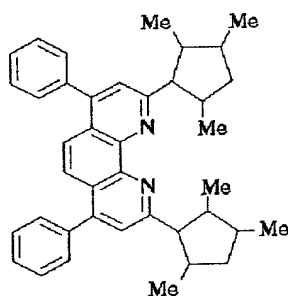
Compound No. 8



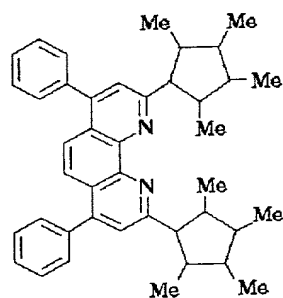
Compound No. 9



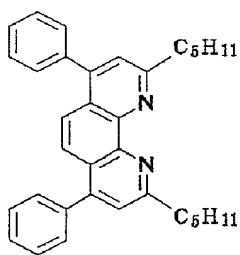
Compound No. 10



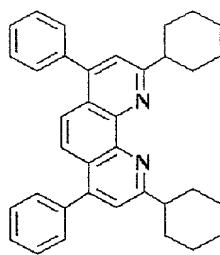
Compound No. 11



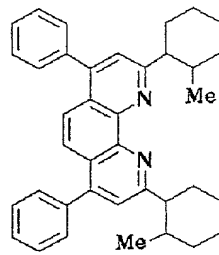
Compound No. 12



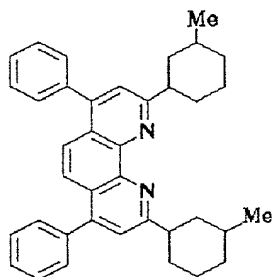
Compound No.13



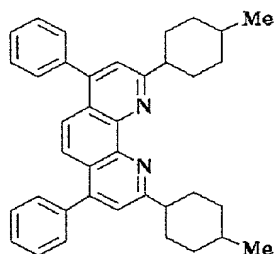
Compound No.14



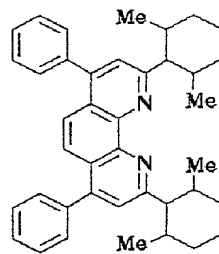
Compound No.15



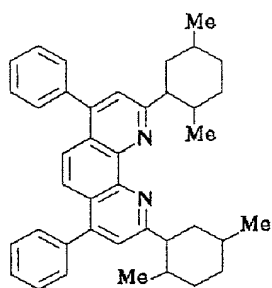
Compound No.16



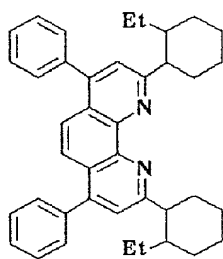
Compound No.17



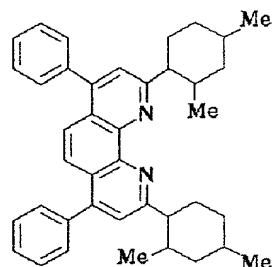
Compound No.18



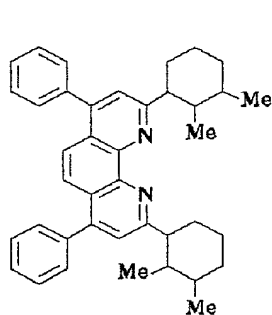
Compound No.19



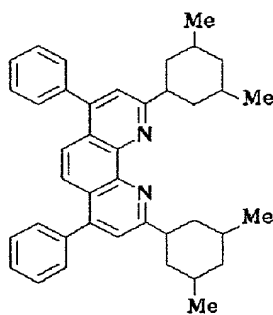
Compound No.20



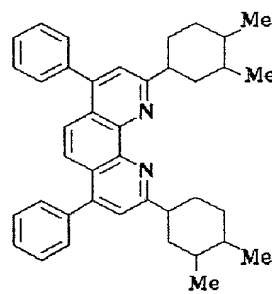
Compound No.21



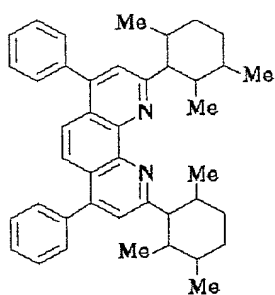
Compound No.22



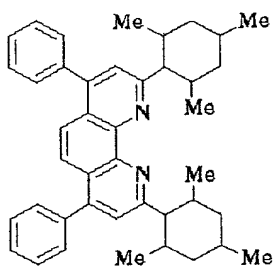
Compound No.23



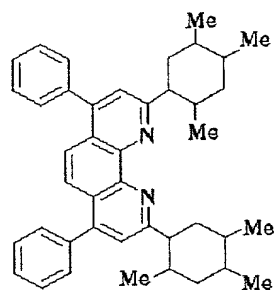
Compound No.24



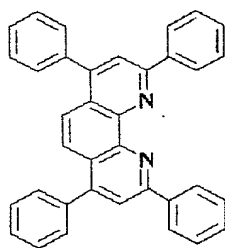
Compound No. 25



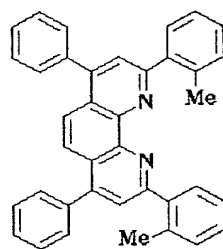
Compound No. 26



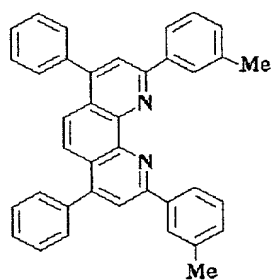
Compound No. 27



Compound No. 28

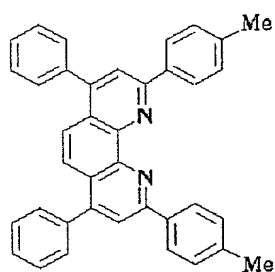


Compound No. 29

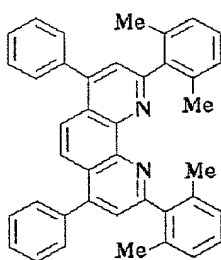


Compound No. 30

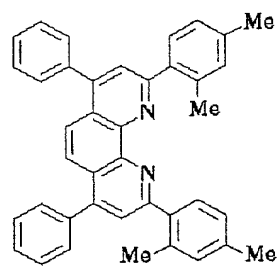
00201T" 89640660



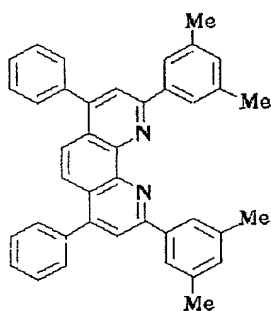
Compound No.31



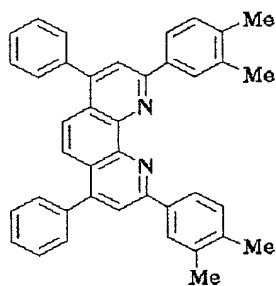
Compound No.32



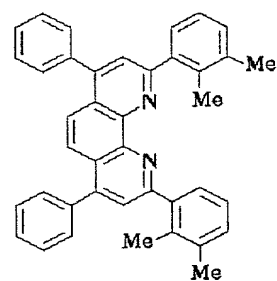
Compound No.33



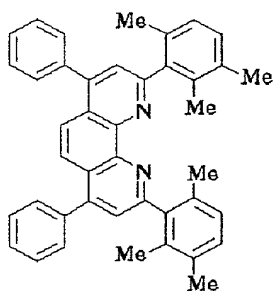
Compound No.34



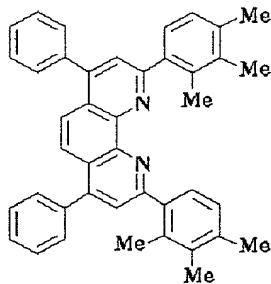
Compound No.35



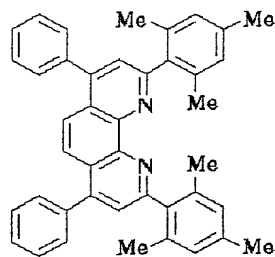
Compound No.36



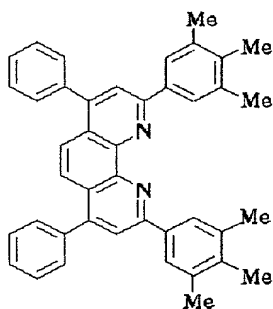
Compound No. 37



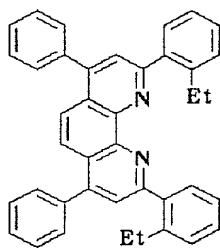
Compound No. 38



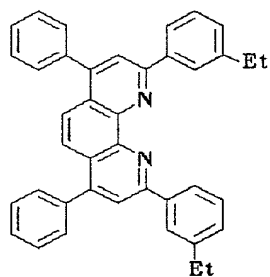
Compound No. 39



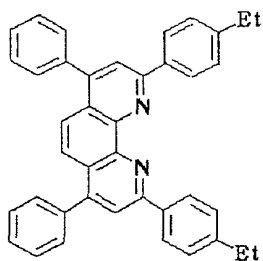
Compound No. 40



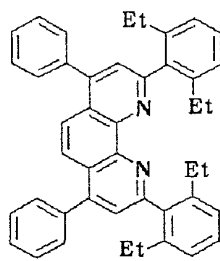
Compound No. 41



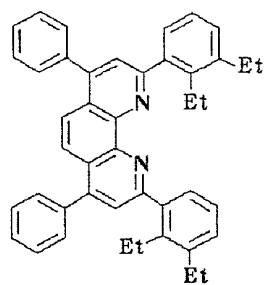
Compound No. 42



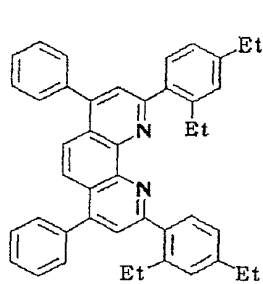
Compound No. 43



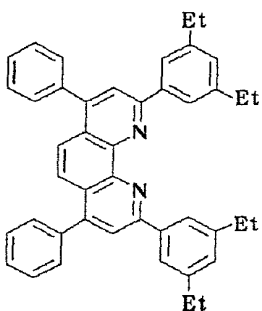
Compound No. 44



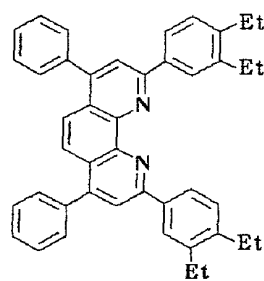
Compound No. 45



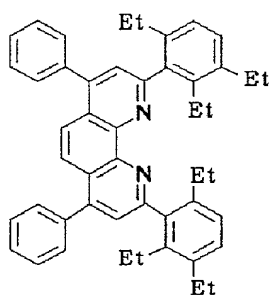
Compound No. 46



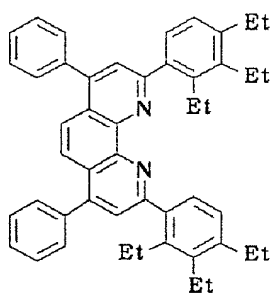
Compound No. 47



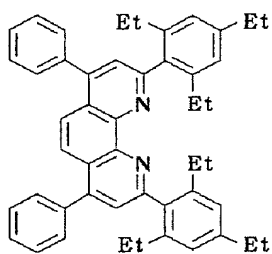
Compound No. 48



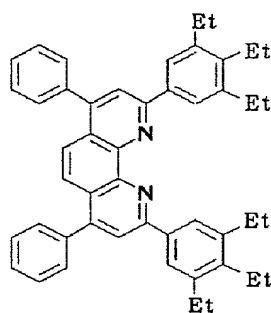
Compound No. 49



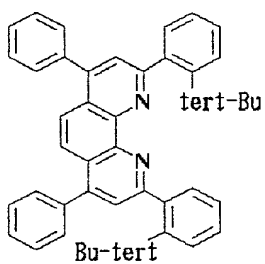
Compound No. 50



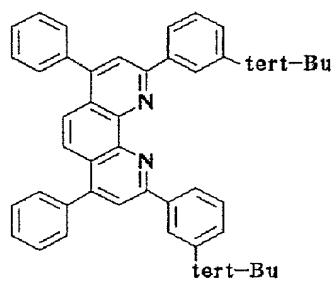
Compound No. 51



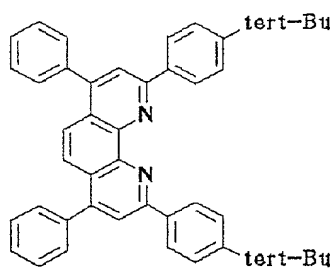
Compound No. 52



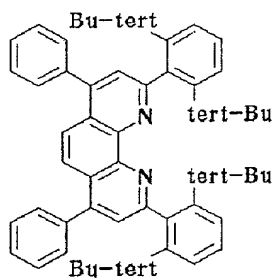
Compound No. 53



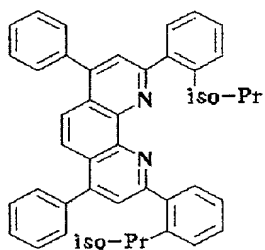
Compound No. 54



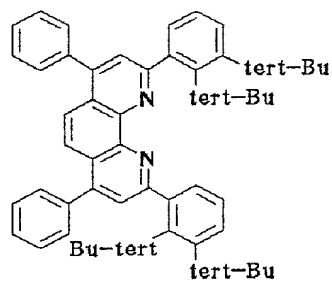
Compound No. 55



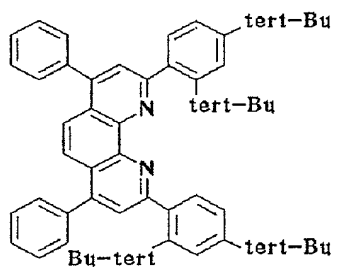
Compound No. 56



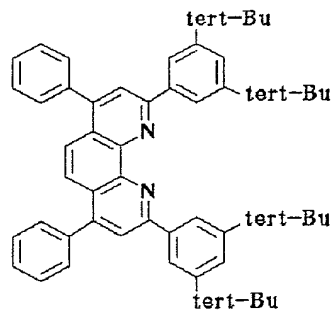
Compound No. 57



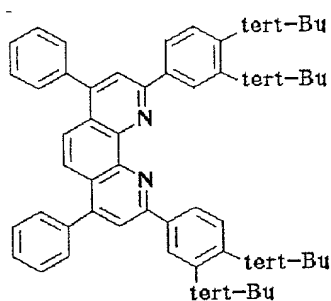
Compound No. 58



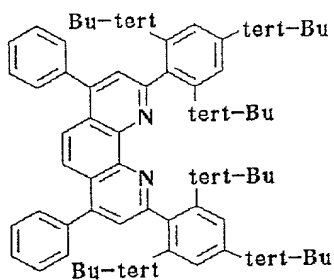
Compound No. 59



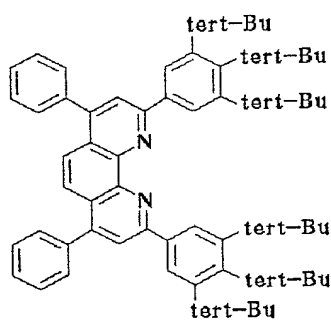
Compound No. 60



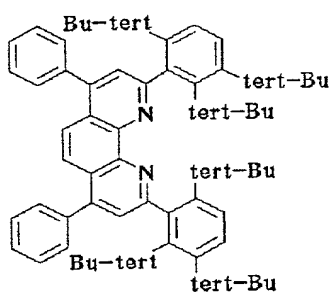
Compound No. 61



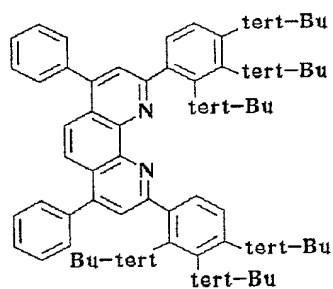
Compound No. 62



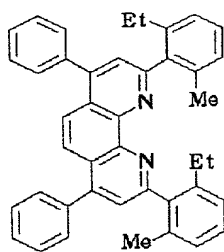
Compound No. 63



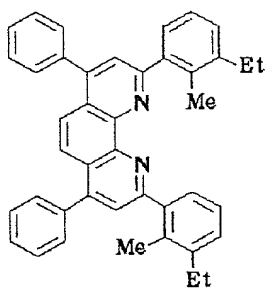
Compound No. 64



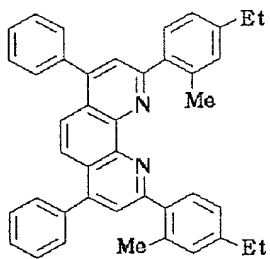
Compound No. 65



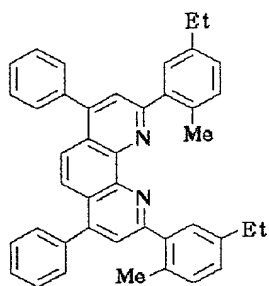
Compound No. 66



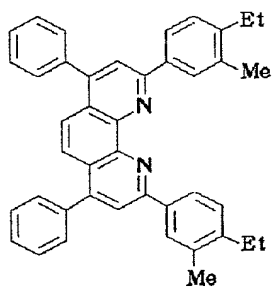
Compound No.67



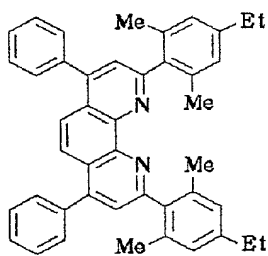
Compound No.68



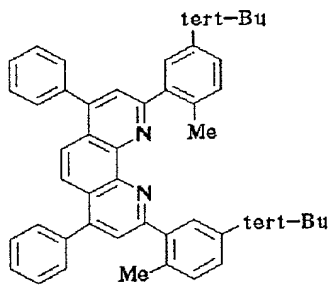
Compound No.69



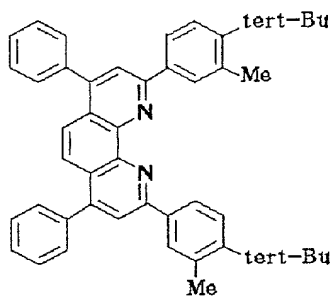
Compound No.70



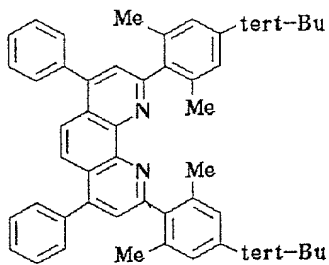
Compound No.71



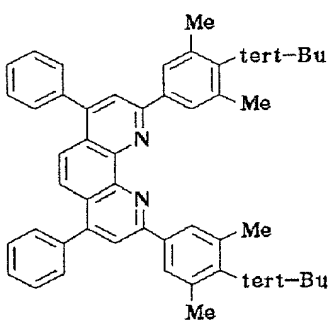
Compound No.72



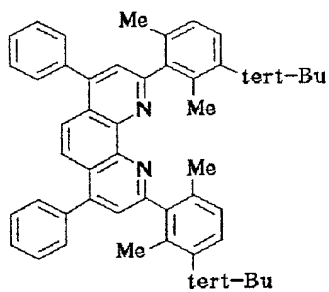
Compound No. 73



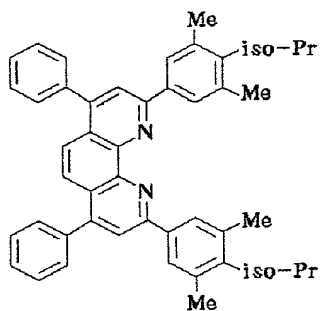
Compound No. 74



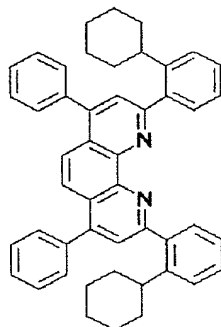
Compound No. 75



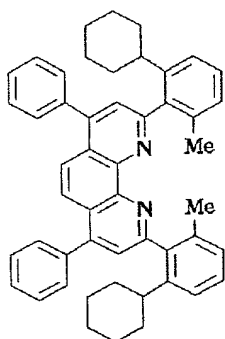
Compound No. 76



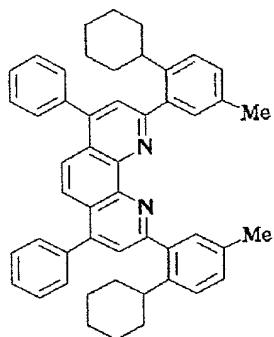
Compound No. 77



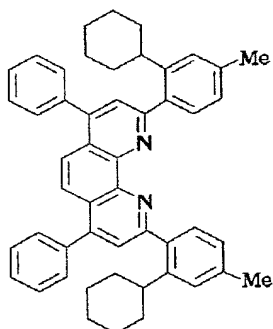
Compound No. 78



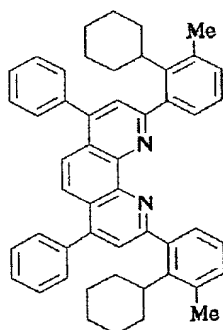
Compound No. 79



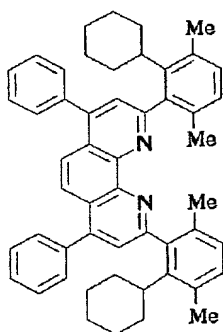
Compound No. 80



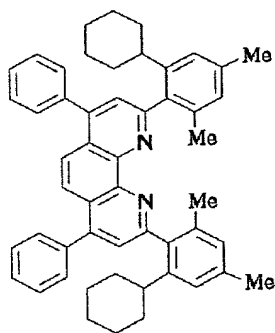
Compound No. 81



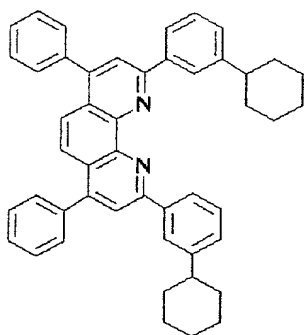
Compound No. 82



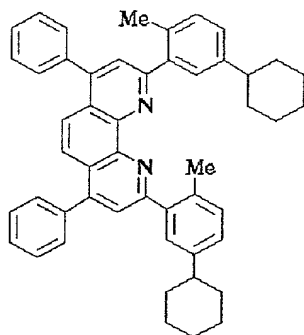
Compound No. 83



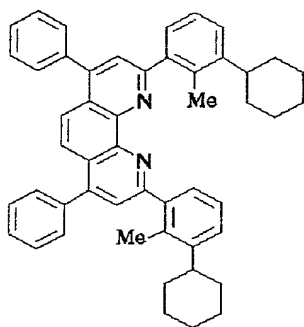
Compound No. 84



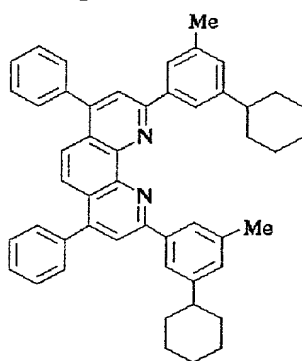
Compound No. 85



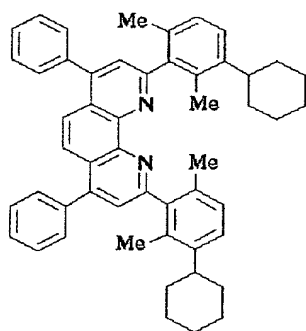
Compound No. 86



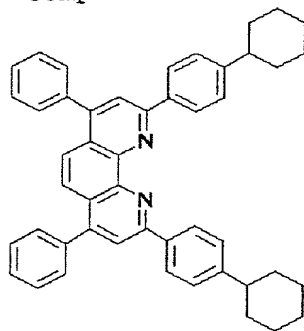
Compound No. 87



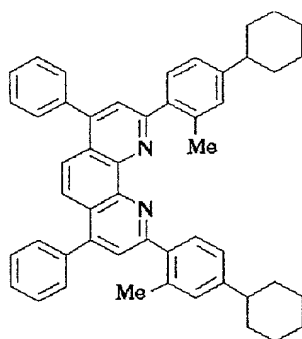
Compound No. 88



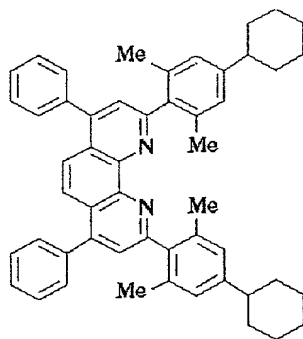
Compound No. 89



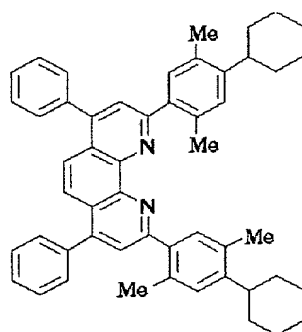
Compound No. 90



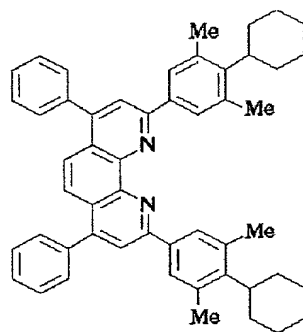
Compound No. 91



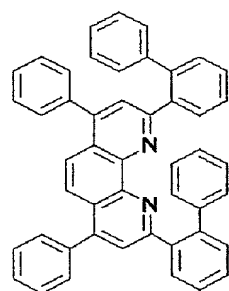
Compound No. 92



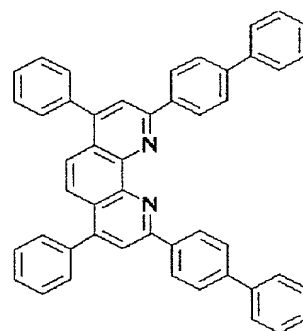
Compound No. 93



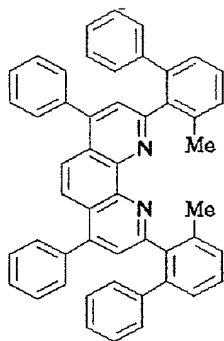
Compound No. 94



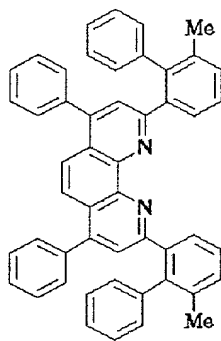
Compound No. 95



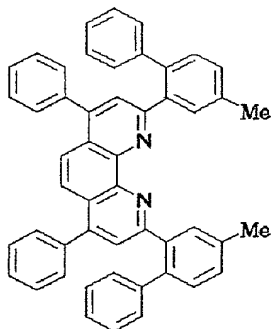
Compound No. 96



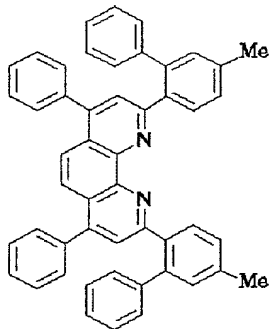
Compound No. 97



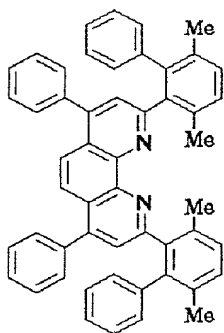
Compound No. 98



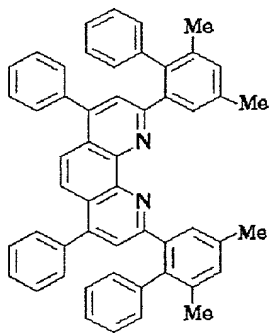
Compound No. 99



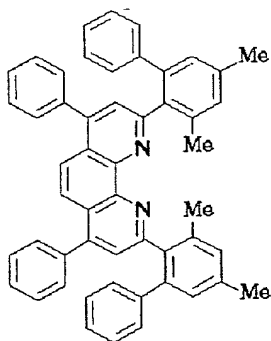
Compound No. 100



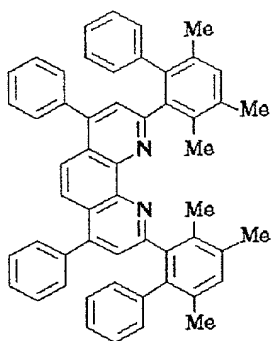
Compound No. 101



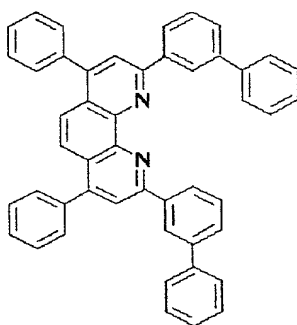
Compound No. 102



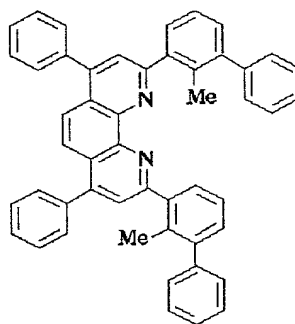
Compound No.103



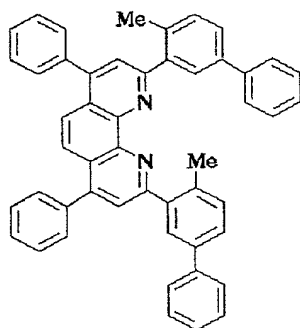
Compound No.104



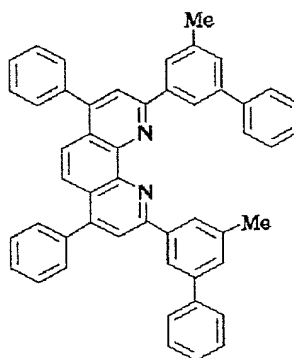
Compound No.105



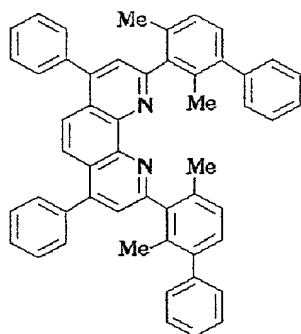
Compound No.106



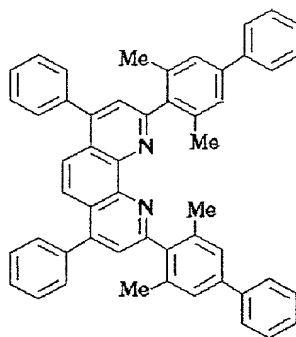
Compound No.107



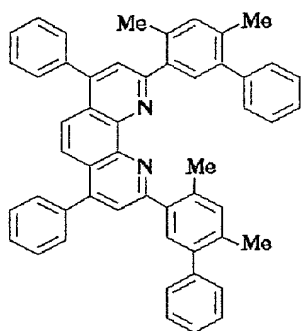
Compound No.108



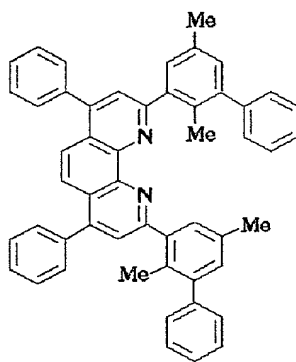
Compound No. 109



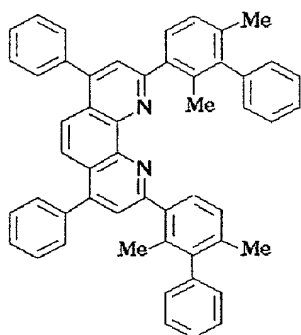
Compound No. 110



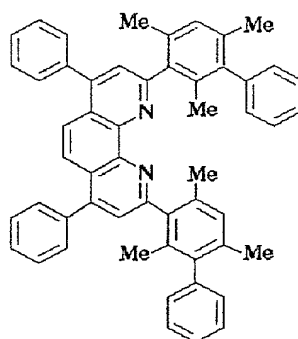
Compound No. 111



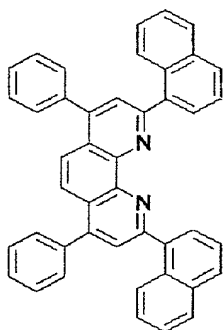
Compound No. 112



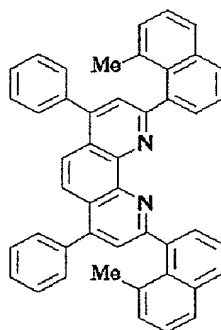
Compound No.113



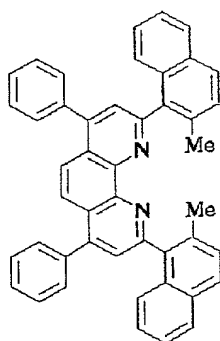
Compound No.114



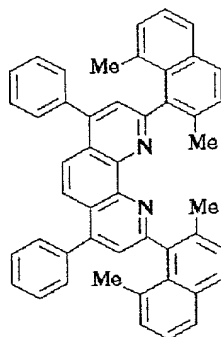
Compound No.115



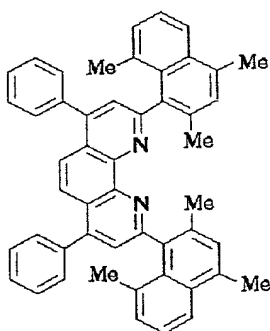
Compound No.116



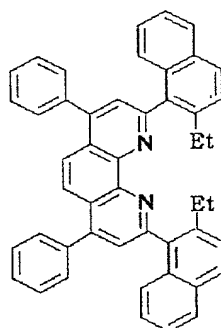
Compound No.117



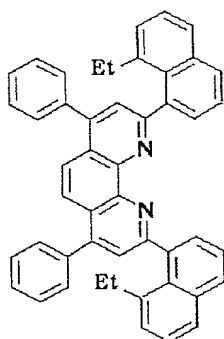
Compound No.118



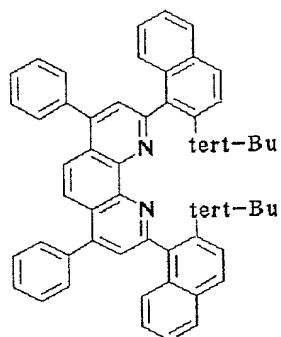
Compound No.119



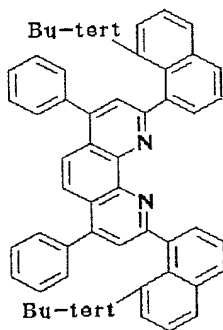
Compound No.120



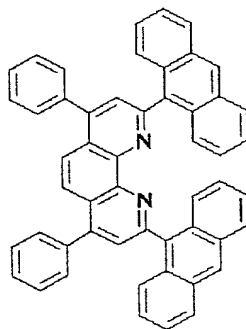
Compound No.121



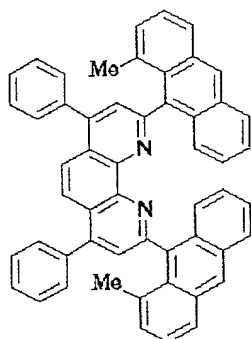
Compound No.122



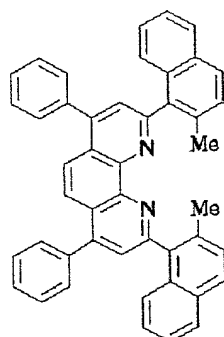
Compound No.123



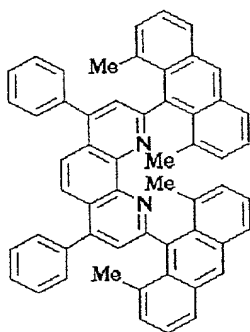
Compound No.124



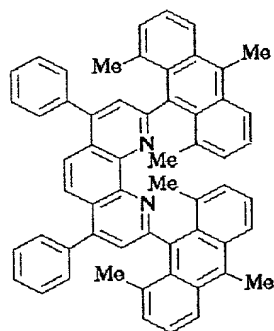
Compound No.125



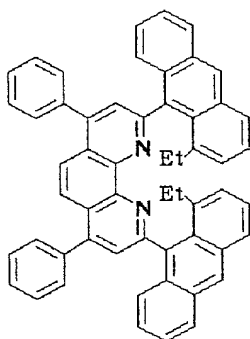
Compound No.126



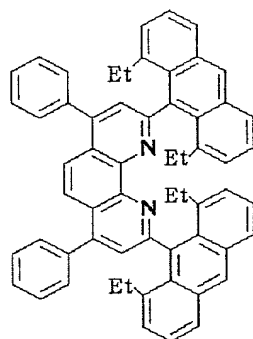
Compound No.127



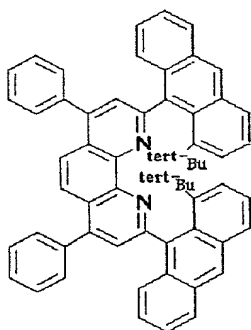
Compound No.128



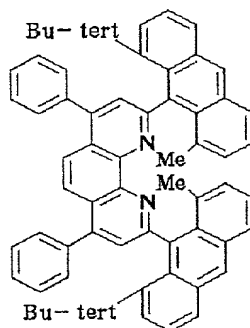
Compound No.129



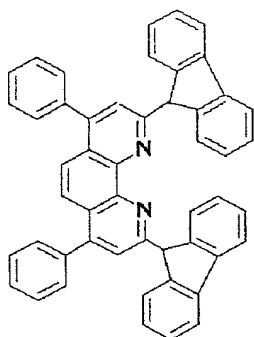
Compound No.130



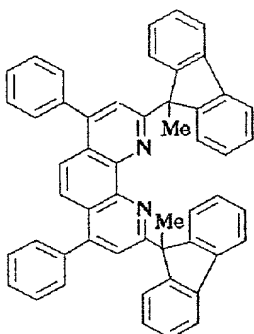
Compound No.131



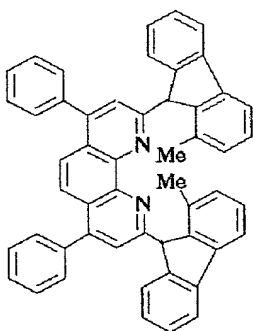
Compound No.132



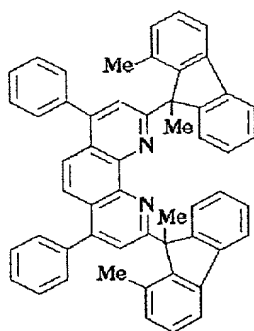
Compound No.133



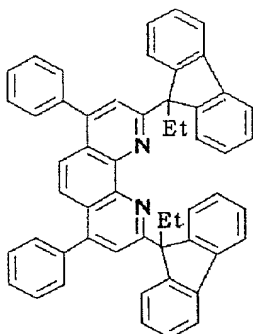
Compound No.134



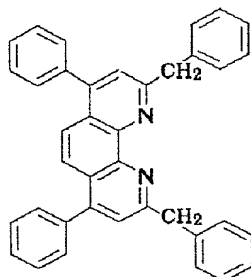
Compound No.135



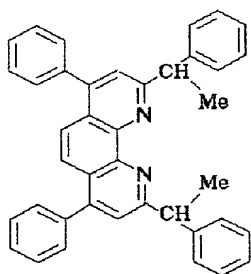
Compound No.136



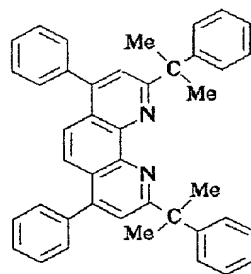
Compound No.137



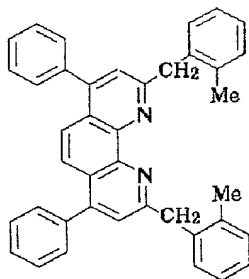
Compound No.138



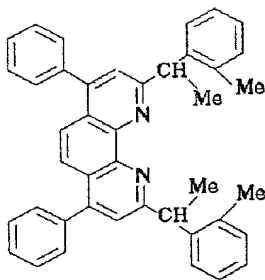
Compound No.139



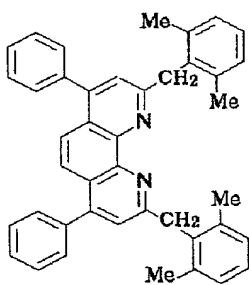
Compound No.140



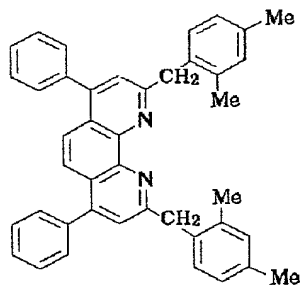
Compound No.141



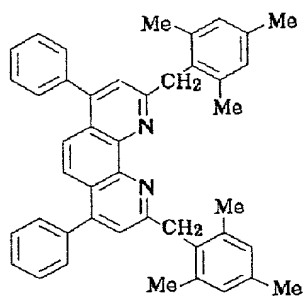
Compound No.142



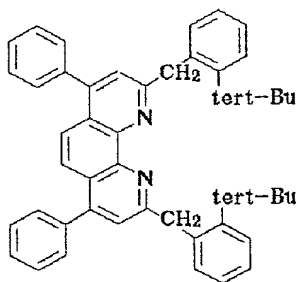
Compound No.143



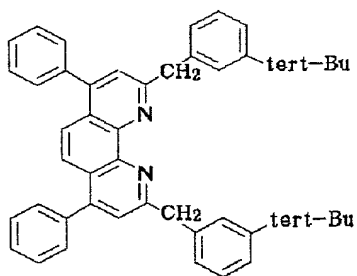
Compound No.144



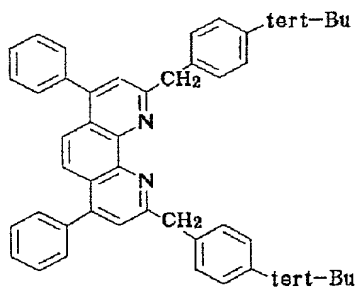
Compound No.145



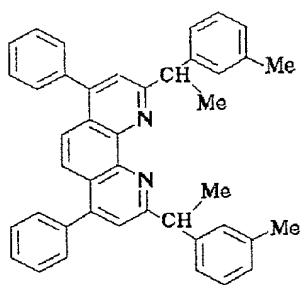
Compound No.146



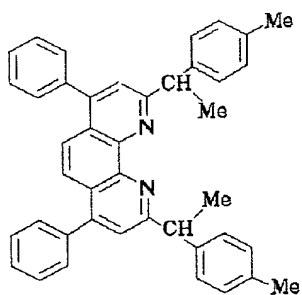
Compound No.147



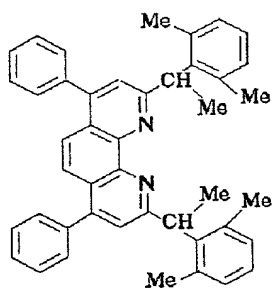
Compound No.148



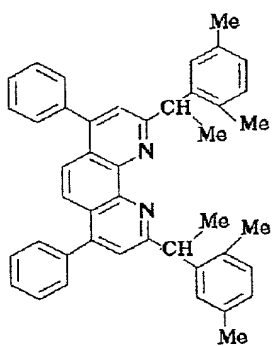
Compound No.149



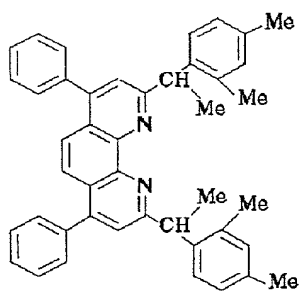
Compound No.150



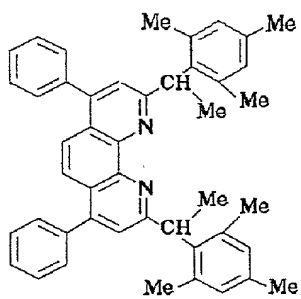
Compound No.151



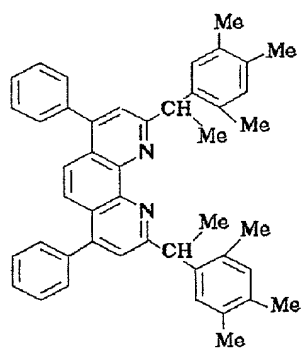
Compound No.152



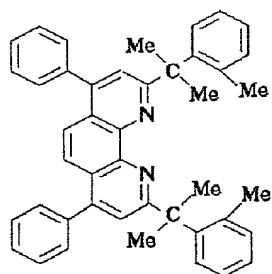
Compound No.153



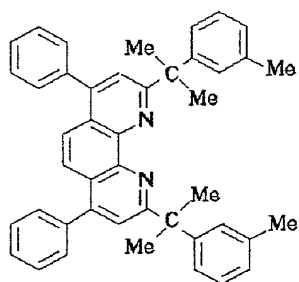
Compound No.154



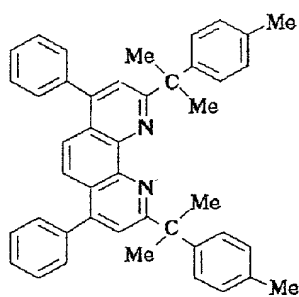
Compound No.155



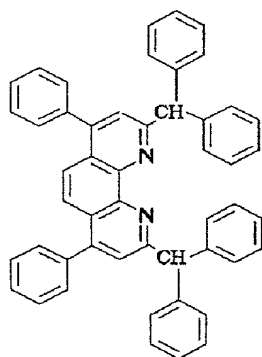
Compound No.156



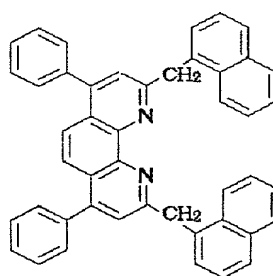
Compound No.157



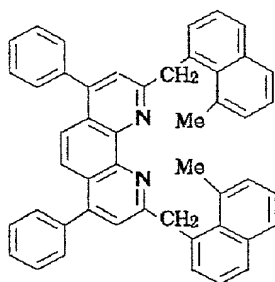
Compound No.158



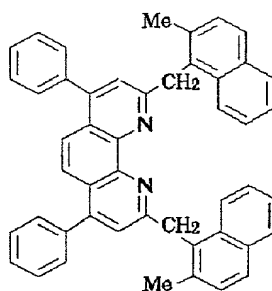
Compound No.159



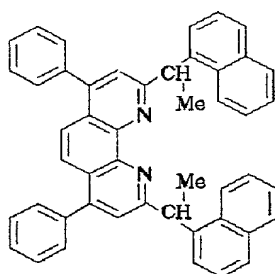
Compound No.160



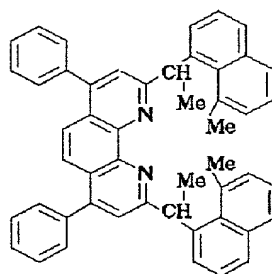
Compound No.161



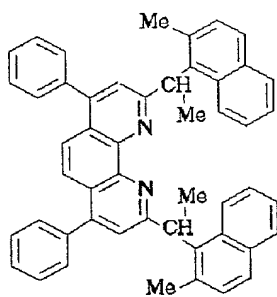
Compound No.162



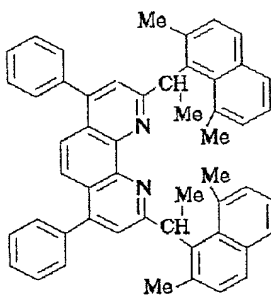
Compound No.163



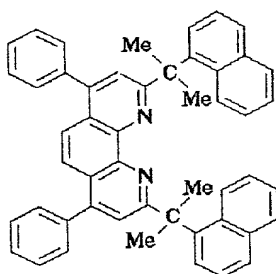
Compound No.164



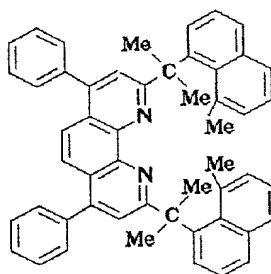
Compound No.165



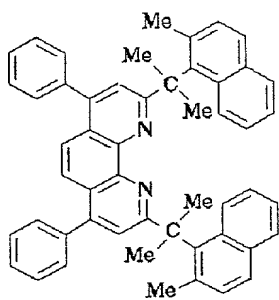
Compound No.166



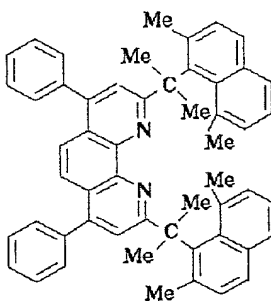
Compound No.167



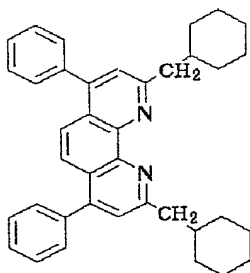
Compound No.168



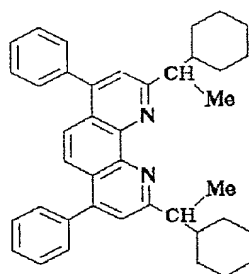
Compound No.169



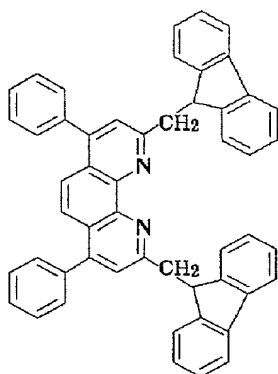
Compound No.170



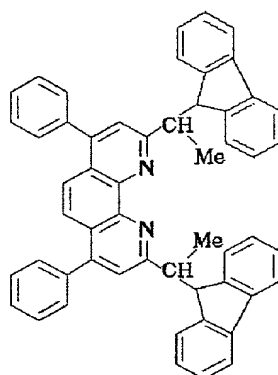
Compound No.171



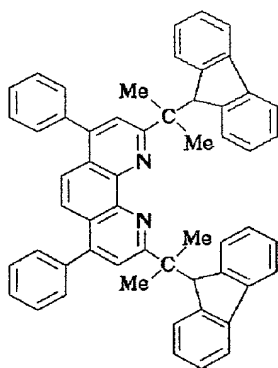
Compound No.172



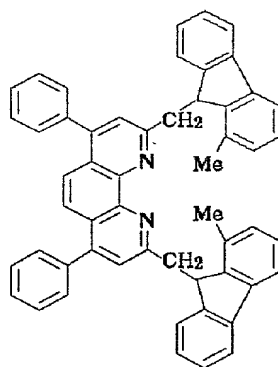
Compound No.173



Compound No.174



Compound No.175



Compound No.176

Compound No.178

<First Embodiment>

In this embodiment, a transparent electrode, made of ITO (indium tin oxide) or Zn-doped indium oxide, is formed on a glass substrate 6 by sputtering or vacuum deposition, followed by successively forming a hole transporting luminescent layer 4a, a hole transporting luminescent layer 4b, a hole-blocking layer 33 containing

00201T-88640/60

a bathophenanthroline (derivative) compound of the afore-
indicated general formula, an electron transport layer 2,
and a cathode electrode 1 in this order according to a
vacuum deposition technique to form an organic EL device
(organic EL device) 21 made of the amorphous organic thin
films.

This organic EL device 21 has such an arrangement
that the hole transport layer 4 serves also as a
luminescent layer, and this fundamental structure is
likewise employed in other embodiments described
hereinafter.

The feature of the organic EL device 21 of this
embodiment resides in that the bathophenanthroline
derivative-containing layer 33 is interposed, as a hole-
blocking layer, between the hole transport layer 4 and
the electron transport layer 2, so that the re-
combination of electrons-holes is promoted in the hole
transport layer 4, at which luminescence is emitted,
and/or luminescence is also emitted from the
bathophenanthroline derivative-containing layer 33.

Fig. 2 schematically shows the built-up structure
of the organic EL device of this embodiment in Fig. 1 as
a band model.

In Fig. 2, the thick lines (L_1 , L_2) indicated at

the cathode 1 made of Al and Al-Li (aluminium-lithium,) and the ITO transparent electrode 5 layer, respectively, mean approximate work functions of the respective metals. In the respective layers between the electrodes, upper thick lines l_1 , l_2 , l_3 and l_4 and numerical values thereof indicate the lowest unoccupied molecular orbital (LUMO) levels, and lower thick lines l_5 , l_6 , l_7 and l_8 and numerical values thereof indicate the highest occupied molecular orbital (HOMO) levels, respectively. It is to be noted that the energy levels in Fig. 2 are shown only by way of example and may widely vary depending on the types of materials.

In the organic EL device, as shown in Fig. 2, the holes h charged from the transparent electrode 5 serving as an anode are moved via the hole transport layer 4. On the other hand, electrons e charged from the metal electrode 1 serving as a cathode are moved via the electron transport layer 2. The electrons-holes are recombined in the hole transporting luminescent layer, at which luminescence is emitted.

The electrons e charged from the metal electrode 1 serving as a cathode has the tendency of moving toward a lower energy level, and can arrive at the hole transporting luminescent layers 4b, 4a via the lowest

unoccupied molecular orbital (LUMO) levels l_1 to l_4 of the respective layers in the order of the metal electrode 1, electron transport layer 2, hole-blocking layer 33, hole transporting luminescent layer 4b and hole transporting luminescent layer 4a.

On the other hand, the holes h charged from the ITO transparent electrode 5 serving as an anode has the tendency of moving toward a higher energy level, and can move to the electron transport layer 2 via the highest occupied molecular orbital (HOMO) levels l_5 to l_7 of the respective layers in the order of the hole transporting luminescent layer 4a, hole transporting luminescent layer 4b and hole-blocking layer 33.

However, as shown in Fig. 2, the highest occupied molecular orbital (HOMO) level l_8 of the electron transport layer 2 is lower in energy than the highest occupied molecular orbital (HOMO) level l_7 of the hole-blocking layer 33. This makes it difficult that the charged holes h moves from the hole-blocking layer 33 toward the electron transport layer 2, and thus, they are filled in the hole-blocking layer 33.

Eventually, the holes h filled in the hole-blocking layer 33 promote the re-combination of electrons-holes at the hole transport layer 4, thereby permitting the

luminescent materials of the hole transporting luminescent layers 4a, 4b or the hole transport layer 4 to emit luminescence or light.

In this way, the provision of the hole-blocking layer 33 effectively controls the transport of the holes h in the hole-blocking layer 33 so that the electron-hole re-combination in the hole transport layer 4 is efficiently caused. Thus, light with a specific wavelength (blue) is emitted in the form of light emission mainly from the hole transporting luminescent layer 4b, adjoining to the hole-blocking layer 33, of the light-emitting hole transporting luminescent layers 4a, 4b, to which emission from the hole transporting luminescent layer 4a is added.

Fundamentally, the electron-hole re-combination takes place in the respective layers including the electron transport layer 2 and the hole transport layer 4 as resulting from the charge of electrons from the cathode electrode 1 and the charge of holes from the anode electrode 5. Accordingly, in the absence of such a hole-blocking layer 33 as set out above, the electron-hole re-combination occurs at the interface between the electron transport layer 2 and the hole transport layer 4 so that light emission with a long wavelength alone is

obtained. However, when the hole-blocking layer 33 as in this embodiment is provided, it is enabled to promote blue light emission while permitting the luminescent substance-containing hole transport layer 4 as an emission region.

As set out above, the hole-blocking layer 33 is provided to control the transport of the holes h. To this end, it is sufficient that the highest occupied molecular orbital (HOMO) level of the hole-blocking layer 33 is not higher than the HOMO level that is lower in energy between the HOMO levels of the hole transporting luminescent layer 4b and the electron transport layer 2, and that the lowest unoccupied molecular orbital (LUMO) level of the hole-blocking layer 33 is not lower than the LUMO level that is lower in energy and is not higher than the LUMO level that is higher in energy, between the LUMO levels of the hole transporting luminescent layer 4b and the electron transport layer 2. Thus, the invention is not limited to such an arrangement as set out before.

In the practice of the invention, the energy levels may not always be within such ranges as defined before, and the bathophenanthroline compound-containing layer per se may emit light or luminescence. In addition, the hole-blocking layer may be made of a built-up structure

including a plurality of layers.

The hole-blocking layer 33 may be formed of the bathophenanthroline derivative and/or other material, and its thickness may be changed within a range permitting its function to be maintained. More particularly, the thickness is preferably within a range of 1 Å to 1,000 Å (0.1 nm to 100 nm). If the thickness is too small, the hole blocking ability becomes incomplete, so that the re-combination region is liable to extend over the hole transport layer and the electron transport layer. On the contrary, when the thickness is too large, light emission may not occur due to the increase in film resistance.

The organic EL device 21 is made by use of a vacuum deposition apparatus 11 shown in Fig. 3. The apparatus 11 has therein a pair of support means 13 fixed below an arm 12. A stage mechanism (not shown) is provided between the fixed support means 13 so that a transparent glass substrate 6 can be turned down and a mask 22 can be set as shown. Below the glass substrate 6 and the mask 22, a shutter 14 supported with a shaft 14a is provided, below which a given number of deposition sources 28 are further provided. The deposition sources are heated by means of a resistance heating system using an electric power supply 29. For the heating, an EB (electron beam) heating system

may also be used, if necessary.

In this apparatus, the mask 22 is for pixels, and the shutter 14 is for deposition materials. The shutter 14 is able to rotate about the shaft 14a and has the function of intercepting a deposition stream of a material depending on the sublimation temperature of the deposition material.

Fig. 4 is a plan view showing a specific example of the organic EL device fabricated by use of the vacuum deposition apparatus. More particularly, ITO transparent electrodes 5 each with a size of 2 mm × 2 mm are vacuum deposited on a glass substrate 6 with a size, L, of 30 mm × 30 mm by means of the vacuum deposition apparatus in a thickness of about 100 nm, followed by vacuum deposition of SiO₂ 30 over the entire surface thereof and etching in a given pixel pattern to form a multitude of openings 31. In this way, the transparent electrodes 5 are, respectively, exposed. Thereafter, the respective organic layers 4, 33, 2 and a metal electrode 1 are successively formed through a deposition mask 22 of SiO₂ on each 2 mm × 2 mm emission region (pixel) PX.

Using the vacuum deposition apparatus 11, a large-sized pixel may be singly formed, aside from the device having a multitude of pixels as shown in Fig. 4.

In this way, when the organic layer 33 is formed in order to improve the efficiency of the electron-hole recombinations in the emission region, there can be obtained an organic EL device that is stable and high in brightness, can be driven at a low voltage and has the hole transporting luminescent layer 4. As will be described in more detail, it is enabled to obtain a brightness of not smaller than $10,000 \text{ cd/m}^2$ by DC drive and a peak brightness, calculated as DC, of not smaller than $55,000 \text{ cd/m}^2$ by pulse drive at a duty ratio of 1/10 with respect to blue light emission.

The transparent electrode, organic hole transport layer, organic hole-blocking layer, organic electron transport layer and metal electrode of the electroluminescent device may, respectively, have a built-up structure made of a plurality of layers.

The respective organic layers of the electroluminescent device may be formed not only by vacuum deposition, but also other film-forming techniques using sublimation or vaporization, or a technique of spin coating, casting or the like.

The hole transporting luminescent layer of the electroluminescent device may be formed by co-deposition of a small amount of molecules in order to control

emission spectra of the device, and may be, for example, an organic thin film containing a small amount of an organic substance such as a perylene derivative, a coumarin derivative or the like.

Usable hole transport materials include, aside from benzidine or its derivatives, styrylamine or its derivatives and triphenylmethane or its derivatives, porphyrin or its derivatives, triazole or its derivatives, imidazole or its derivatives, oxadiazole or its derivatives, polyarylalkanes or derivatives thereof, phenylenediamine or its derivatives, arylamines or derivatives thereof, oxazole or its derivatives, anthracene or its derivatives, fluorenone or its derivatives, hydrazone or its derivatives, stilbene or its derivatives, or heterocyclic conjugated monomers, oligomers, polymers and the like such as polysilane compounds, vinylcarbazole compounds, thiophene compounds, aniline compounds and the like.

More particularly, mention is made of α -naphthylphenyldiamine, porphyrin, metal tetraphenylporphyrins, metal naphthalocyanines, 4,4',4''-trimethyltriphenylamine, 4,4',4''-tris(3-methylphenylphenylamino)triphenylamine, N,N,N',N'-tetrakis(p-tolyl)-p-phenylenediamine, N,N,N',N'-

002011" 29640250

tetraphenyl-4,4'-diaminobiphenyl, N-phenylcarbazole, 4-di-p-tolylaminostilbene, poly(paraphenylenevinylene), poly(thiophenevinylene), poly(2,2'-thienylpyrrole) and the like, although not limited thereto.

Usable electron transport materials include quinoline or its derivatives, perylene or its derivatives, bistyllyl or its derivatives, pyrazine or its derivatives, and the like.

More specifically, mention is made, for example, of 8-hydroxyquinoline aluminium, anthracene, naphthalene, phenanthrene, pyrene, chrysene, perylene, butadiene, coumarin, acridine, stilbene, or derivatives thereof.

The materials used as the anode electrode or cathode electrode of the electroluminescent device are not limitative in types.

The cathode electrode material should preferably be made of a metal whose work function from a vacuum level of an electrode material is small in order to efficiently charge electrons. There may be used, aside from an aluminium-lithium alloy, low work function metals such as, for example, aluminium, indium, magnesium, silver, calcium, barium, lithium and the like, singly or in the form of alloys with other metals for enhancing the stability thereof.

002011 2254060

In order to take out organic electroluminescence from the side of the anode electrode, ITO is used as a transparent anode electrode in examples appearing hereinafter. Nevertheless, there may be used electrode materials, which have a great work function from the vacuum level of an anode electrode material and include, for example, gold, a stannic oxide-antimony mixture, a zinc oxide-aluminium mixture or the like, so as to efficiently charge holes.

The substrate 2 may not be limited to a glass substrate, but may be made of an opaque material. More particularly, there may be used, for example, a silicon substrate, a Cr substrate, or a substrate made of glass, on which a metal is formed by vacuum deposition. Where a substrate made of an opaque material is used, it is preferred that the upper surface of an organic EL device (i.e. the side of the cathode electrode) is formed of a transparent or translucent material so that electroluminescence is picked out to outside. ITO may be used for this purpose, for example.

There can be made an organic EL device for full color or multi-color, which is capable of emission of primaries of R, G and B, by proper choice of luminescent materials, not to mention an organic EL device for

monochrome. Besides, the organic EL device of the invention is usable not only for display, but also for light source along with its application to other optical use.

It will be noted that the organic EL device may be sealed with germanium oxide or the like so as to enhance the stability thereof by suppressing the influence of oxygen or the like in air, or may be driven under conditions drawn to vacuum.

<Second Embodiment>

Fig. 5 is a schematic sectional view showing an essential part of an organic EL device according to a second embodiment of the invention. An organic EL device 22 of this embodiment differs from that of Fig. 1 in that the hole transporting luminescent layer 4b is formed on the ITO transparent electrode 5 so that the hole transporting luminescent layer is formed as a single layer.

<Third Embodiment>

Fig. 6 is a schematic sectional view showing an essential part of an organic EL device according to a third embodiment of the invention.

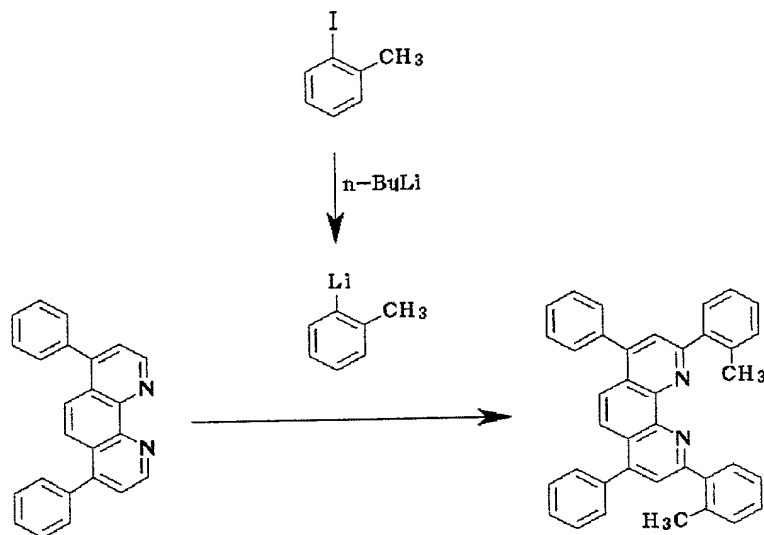
An organic EL device 23 of this embodiment differs from that of Fig. 1 in that a hole transport layer (serving also as a hole transporting luminescent layer) 4a is formed on the ITO transparent electrode 5, and thus, the hole transporting luminescent layer is formed as a single layer, like the second embodiment.

The invention is more particularly described by way of examples.

Example 1

<Preparation of 2,9-di(2-methylphenyl)bathophenanthroline>

The reaction sequence is shown below



n-Butyl lithium (1.6 M n-hexane solution, 17.0 ml,

26.8 mmol) was gradually dropped in an n-hexane solution (40 ml) of 2-iodotoluene (5.84 g, 26.4 mmol) at room temperature. After completion of the dropping, the reaction solution was agitated at room temperature for 16 hours, and the resultant product was separated by filtration, followed by washing of the resulting white solid with n-hexane (40 ml \times 3 times). A toluene solution (50 ml) of bathophenanthroline (2.03 g, 6.11 mmol) was gradually dropped, at room temperature, in an anhydrous diethyl ether/toluene (3:1) solution (20 ml) of the resulting white solid, followed by agitation at room temperature for 16 hours.

60 ml of iced water was added to the resultant reaction solution to separate an organic layer therefrom. The aqueous layer was extracted three times with chloroform, and the resultant organic layer was mixed with the previously separated organic layer. 60 g of manganese dioxide (chemically treated product) was added to the thus mixed organic layer and agitated for 30 minutes, after which 100 g of sodium sulfate was further added, followed by agitation for 30 minutes.

The resulting mixed solution was filtered and concentrated, and the residue was purified through column chromatography (silica gel, developing solvent: n-

hexane/chloroform = 4:1 \rightarrow 2:1), followed by recrystallization (solvent for recrystallization: chloroform/n-hexane = 2:1) to obtain the intended compound (1.01 g, yield: 49.5%) as light yellow crystals.

The product was identified through ^1H -NMR (solvent: chloroform) and FAB-MS measurements.

^1H -NMR: 2.70 (m, 6H, $\text{CH}_3\text{-Ar-}$), 7.25 - 7.75 (s, 18H, aromatic), 7.80 (s, 2H, aromatic), 7.90 (s, 2H, aromatic)

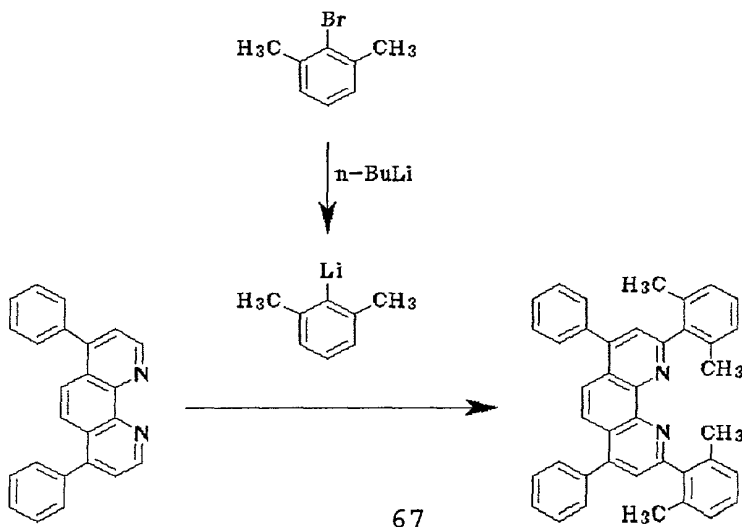
MS: m/s (relative intensity) 512 (M^+ , 100)

The visible light absorption maximum wavelength of a tetrahydrofuran (THF) solution of the product was at 297 nm, with a fluorescent wavelength being at 390 nm.

Example 2

<Preparation of 2,9-di(2,6-dimethylphenyl)-bathophenanthroline>

The reaction sequence is shown below



n-Butyl lithium (1.6 M n-hexane solution, 60.2 ml, 96.3 mmol) was gradually dropped in an n-hexane/anhydrous diethyl ether (10:1) solution (110 ml) of 2-bromo-m-xylene (17.8 g, 96.3 mmol) at room temperature. After completion of the dropping, the reaction solution was heated under reflux for 2 hours and further agitated at room temperature for 16 hours, and the resultant product was separated by filtration, followed by washing of the resulting white solids with n-hexane (50 ml \times 3 times). A toluene solution (80 ml) of bathophenanthroline (5.09 g, 15.3 mmol) was gradually dropped, at room temperature, in an anhydrous diethyl ether solution (40 ml) of the resulting white solids. After completion of the dropping, the solution was heated under reflux for 2 hours and agitated at room temperature for 16 hours.

60 ml of iced water was gradually added to the resultant reaction solution to separate an organic layer therefrom. The aqueous layer was extracted three times with chloroform, and the resultant organic layer was mixed with the previously separated organic layer. 60 g of manganese dioxide (chemically treated product) was added to the thus mixed organic layer and agitated for 30 minutes, after which 100 g of sodium sulfate was further added, followed by agitation for 30 minutes.

The resulting mixed solution was filtered and concentrated, and the residue was purified through column chromatography (silica gel, developing solvent: n-hexane/chloroform = 8:1 \rightarrow 4:1), followed by recrystallization (solvent for recrystallization: chloroform/n-hexane = 2:1) to obtain the intended compound (2.00 g, yield: 39.4%) as light yellow crystals.

The product was identified through ^1H -NMR and FAB-MS measurements.

^1H -NMR: 2.25 (m, 12H, $\text{CH}_3\text{-Ar-}$), 7.05 - 7.25 (s, 6H, aromatic), 7.35 - 7.70 (s, 12H, aromatic), 7.95 (s, 2H, aromatic)

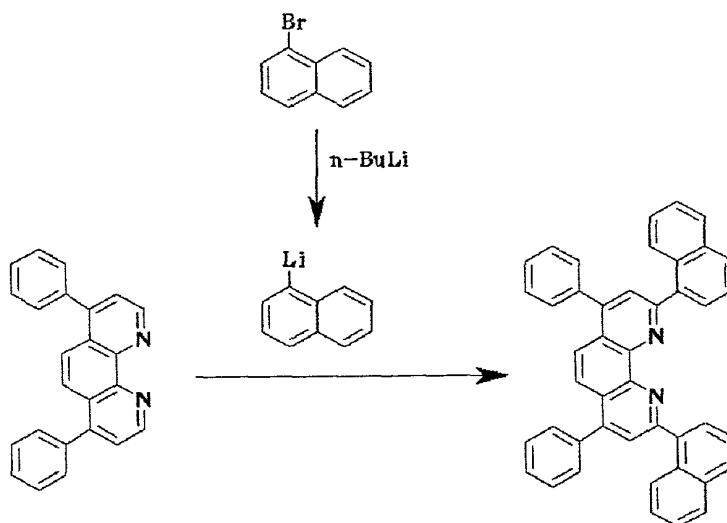
MS: m/s (relative intensity) 540 (M^+ , 100)

The visible light absorption maximum wavelength of a THF solution of the product was at 286 nm, with a fluorescent wavelength being at 380 nm.

Example 3

<Preparation of 2,9-dinaphthyl-bathophenanthroline>

The reaction sequence is shown below



n-Butyl lithium (1.6 M *n*-hexane solution, 15.3 ml, 24.4 mmol) was gradually dropped, at 0°C, in an *n*-hexane/anhydrous diethyl ether (1:1) solution (60 ml) of 1-bromonaphthalene (5.01 g, 24.4 mmol). After completion of the dropping, the reaction solution was agitated at room temperature for 16 hours, and the resultant product was subsequently separated by filtration, and the residue was washed with *n*-hexane (40 ml × 3 times). A toluene solution (80 ml) of bathophenanthroline (2.03 g, 6.11 mmol) was gradually dropped, at room temperature, in an anhydrous diethyl ether solution (40 ml) of the resulting

solids. After completion of the dropping, the reaction solution was agitated at room temperature for 16 hours.

60 ml of iced water was gradually added to the resultant reaction solution to separate an organic layer therefrom. The aqueous layer was extracted three times with chloroform, and the resultant organic layer was mixed with the previously separated organic layer. 60 g of manganese dioxide (chemically treated product) was added to the thus mixed organic layer and agitated for 30 minutes, after which 100 g of sodium sulfate was further added, followed by agitation for 30 minutes.

The resulting mixed solution was filtered and concentrated, and the residue was purified through column chromatography (silica gel, developing solvent: n-hexane/chloroform = 8:1 \rightarrow 4:1), followed by recrystallization (solvent for recrystallization: chloroform/n-hexane = 2:1) to obtain the intended compound (1.38 g, yield: 68.2%).

The product was identified through ^1H -NMR and FAB-MS measurements.

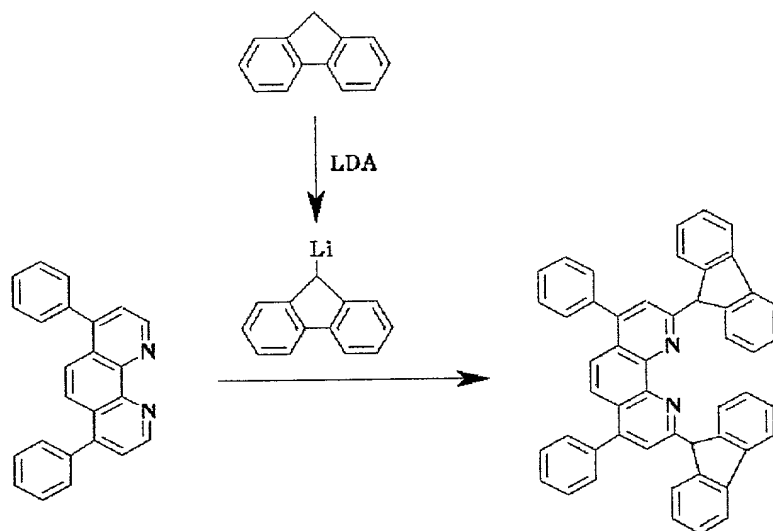
^1H -NMR: 7.30 - 8.00 (s, 24H, aromatic), 8.32 (s, 2H, aromatic), 8.68 (s, 2H, aromatic)

MS: m/s (relative intensity) 584 (M^+ , 100)

Example 4

<Preparation of 2,9-difluorenyl-bathophenanthroline>

The reaction sequence is shown below



Lithium diisopropylamine (LDA) (1.89 g, 17.4 mmol) was added to a THF solution (30 ml) of fluorene (4.16 g, 25.0 mmol) and agitated at room temperature for 16 hours. Thereafter, the THF and diisopropylamine were removed by distillation under reduced pressure. A toluene solution (60 ml) of bathophenanthroline (2.03 g, 6.11 mmol) was gradually dropped in an anhydrous diethyl ether solution (20 ml) of the resultant yellow solids at room temperature. After the dropping, the reaction solution was heated under reflux for 2 hours and agitated at room temperature for 16 hours.

09704958 110200

60 ml of iced water was gradually added to the resultant reaction solution to separate an organic layer therefrom. The aqueous layer was extracted three times with chloroform, and the resultant organic layer was mixed with the previously separated organic layer. 60 g of manganese dioxide (chemically treated product) was added to the thus mixed organic layer and agitated for 30 minutes, after which 100 g of sodium sulfate was further added, followed by agitation for 30 minutes.

The resulting mixed solution was filtered and concentrated, and the residue was purified through column chromatography (silica gel, developing solvent: n-hexane/chloroform = 8:1 \rightarrow 4:1), followed by recrystallization (solvent for recrystallization: chloroform/n-hexane = 2:1) to obtain the intended compound (1.38 g, yield: 68.2%).

The product was identified through ^1H -NMR and FAB-MS measurements.

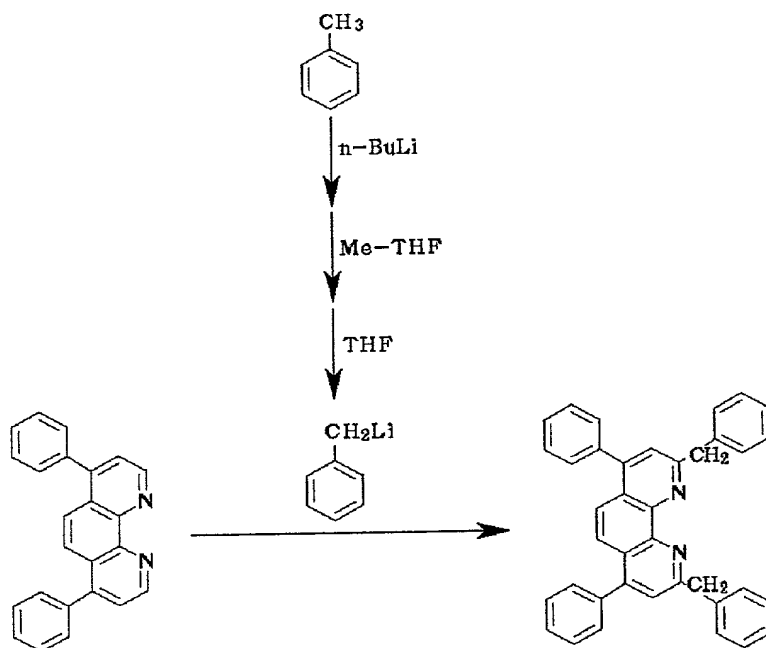
^1H -NMR: 4.51 (m, 2H, Ar-CH₂-Ar), 7.30 - 7.78 (s, 28H, aromatic), 7.81 (s, 2H, aromatic)

MS: m/s (relative intensity) 660 (M⁺, 100)

Example 5

<Preparation of 2,9-dibenzyl-bathophenanthroline>

The reaction sequence is shown below



n -Butyl lithium (1.6 M n -hexane solution, 4.45 ml, 7.13 mmol) was gradually dropped in anhydrous toluene (2.24 g, 24.9 mmol) at room temperature. After completion of the dropping, Me-THF (0.627 g, 7.47 mmol) was further added to the solution at -22°C in 20 minutes. Thereafter, THF (1.06 g, 14.7 mmol) was added to in 30 minutes, followed by agitation at 6 to 10°C for 16 hours. A toluene solution (40 ml) of bathophenanthroline (2.03 g, 6.11 mmol) was gradually dropped, at room temperature, in

the resultant reaction solution. After completion of the dropping, the reaction solution was agitated at room temperature for 16 hours.

60 ml of iced water was gradually added to the resultant reaction solution to separate an organic layer therefrom. The aqueous layer was extracted three times with chloroform, and the resultant organic layer was mixed with the previously separated organic layer. 60 g of manganese dioxide (chemically treated product) was added to the thus mixed organic layer and agitated for 30 minutes, after which 100 g of sodium sulfate was further added, followed by agitation for 30 minutes.

The resulting mixed solution was filtered and concentrated, and the residue was purified through column chromatography (silica gel, developing solvent: n-hexane/chloroform = 8:1 \rightarrow 4:1), followed by recrystallization (solvent for recrystallization: chloroform/n-hexane = 2:1) to obtain the intended compound (0.88 g, yield: 43.3%).

The product was identified through ^1H -NMR and FAB-MS measurements.

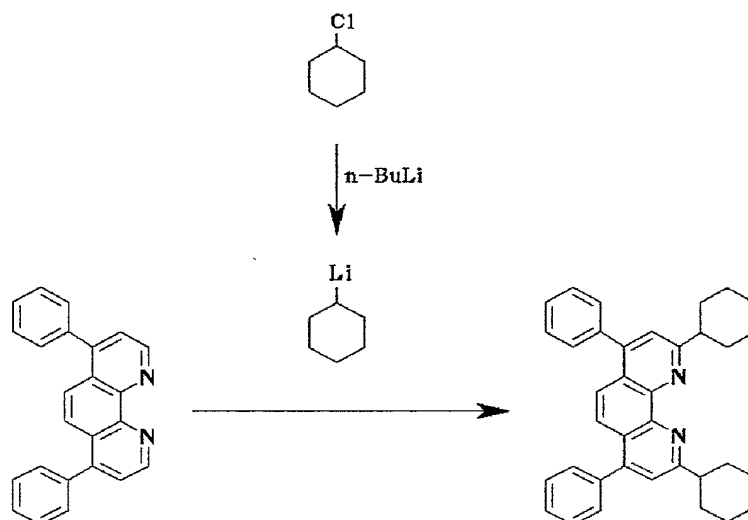
^1H -NMR: 4.68 (m, 4H, $-\text{CH}_2-\text{Ar}$), 7.28 - 7.78 (s, 22H, aromatic), 7.81 (s, 2H, aromatic)

MS: m/s (relative intensity) 512 (M^+ , 100)

Example 6

<Preparation of 2,9-dicyclohexyl-bathophenanthroline>

The reaction sequence is shown below



n-Butyl lithium (1.6 M *n*-hexane solution, 36.3 ml, 58.0 mmol) was gradually dropped, at room temperature, in an *n*-hexane/anhydrous diethyl ether (10:1) solution (50 ml) of chlorocyclohexane (3.00 g, 25.0 mmol). After completion of the dropping, the reaction solution was further agitated at room temperature for 16 hours, and the resultant product was subsequently separated by filtration, and the resulting white solids were washed with *n*-hexane (50 ml × 3 times). A toluene solution (40 ml) of bathophenanthroline (2.03 g, 6.11 mmol) was gradually dropped, at room temperature, in an anhydrous

diethyl ether solution (10 ml) of the resulting white solids. After completion of the dropping, the reaction solution was agitated at room temperature for 16 hours.

60 ml of iced water was gradually added to the resultant reaction solution to separate an organic layer therefrom. The aqueous layer was extracted three times with chloroform, and the resultant organic layer was mixed with the previously separated organic layer. 60 g of manganese dioxide (chemically treated product) was added to the thus mixed organic layer and agitated for 30 minutes, after which 100 g of sodium sulfate was further added, followed by agitation for 30 minutes.

The resulting mixed solution was filtered and concentrated, and the residue was purified through column chromatography (silica gel, developing solvent: n-hexane/chloroform = 8:1 \rightarrow 4:1), followed by recrystallization (solvent for recrystallization: chloroform/n-hexane = 2:1) to obtain the intended compound (0.98 g, yield: 48.3%).

The product was identified through ^1H -NMR and FAB-MS measurements.

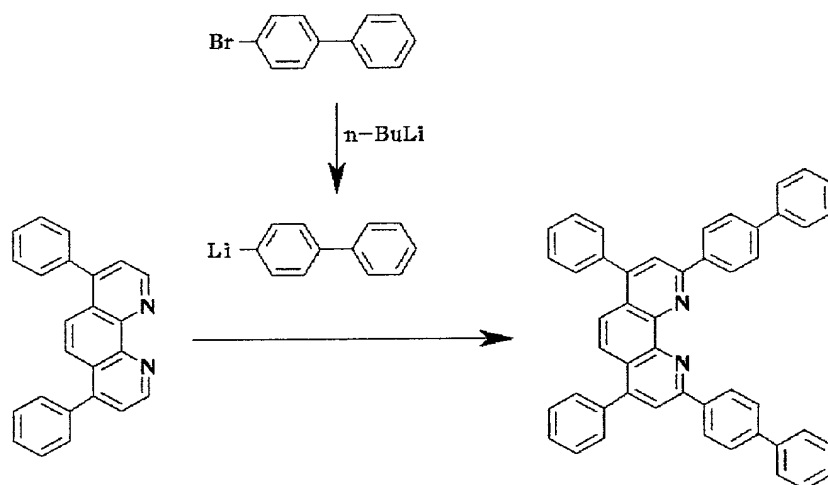
^1H -NMR: 0.80 - 2.45 (m, 20H, $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-$), 3.20 (m, 2H, $-\text{CH}-\text{Ar}$), 7.25 - 7.75 (s, 12H, aromatic), 7.81 (s, 2H, aromatic)

MS: m/s (relative intensity) 496 (M^+ , 100)

Example 7

<Preparation of 2,9-dibiphenyl-bathophenanthroline>

The reaction sequence is shown below



n-Butyl lithium (1.6 M n-hexane solution, 17.0 ml, 27.2 mmol) was gradually dropped, at room temperature, in an n-hexane/anhydrous diethyl ether (10:1) solution (110 ml) of 4-bromobiphenyl (6.33 g, 27.2 mmol). After completion of the dropping, the reaction solution was agitated at room temperature for 16 hours, and the resultant product was subsequently separated by filtration, and the resulting white solids were washed with n-hexane (50 ml \times 3 times). A toluene solution (40 ml) of bathophenanthroline (2.03 g, 6.11 mmol) was

gradually dropped, at room temperature, in an anhydrous diethyl ether solution (20 ml) of the resulting white solids. After completion of the dropping, the reaction solution was agitated at room temperature for 16 hours.

60 ml of iced water was gradually added to the resultant reaction solution to separate an organic layer therefrom. The aqueous layer was extracted three times with chloroform, and the resultant organic layer was mixed with the previously separated organic layer. 60 g of manganese dioxide (chemically treated product) was added to the thus mixed organic layer and agitated for 30 minutes, after which 100 g of sodium sulfate was further added, followed by agitation for 30 minutes.

The resulting mixed solution was filtered and concentrated, and the residue was purified through column chromatography (silica gel, developing solvent: n-hexane/chloroform = 8:1 \rightarrow 4:1), followed by recrystallization (solvent for recrystallization: chloroform/n-hexane = 2:1) to obtain the intended compound (0.76 g, yield: 37.4%).

The product was identified through ^1H -NMR and FAB-MS measurements.

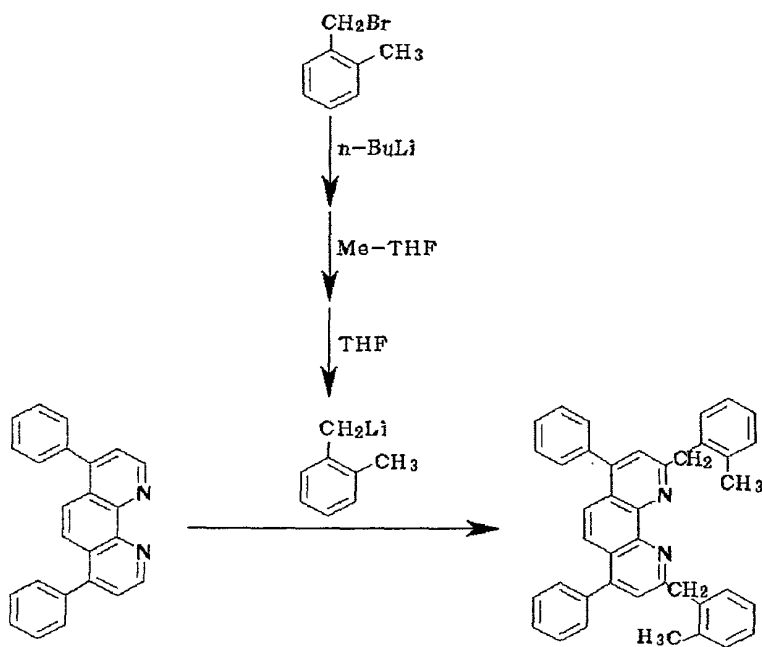
^1H -NMR: 7.25 - 7.78 (s, 26H, aromatic), 7.81 (s, 2H, aromatic), 8.32 (s, 4H, aromatic)

MS: m/s (relative intensity) 636 (M^+ , 100)

Example 8

<Preparation of 2,9-di(2-methylbenzyl)-
bathophenanthroline>

The reaction sequence is shown below



n -Butyl lithium (1.6 M n -hexane solution, 4.45 ml, 7.13 mmol) was gradually dropped in α -bromo- o -xylene (4.91 g, 24.9 mmol) at room temperature. After completion of the dropping, Me-THF (0.627 g, 7.47 mmol) was added in 20 minutes at -22°C , after which THF (1.06 g, 14.7 mmol) was further added in 30 minutes, followed by further

agitation at 6 to 10°C for 16 hours. A toluene solution (40 ml) of bathophenanthroline (2.03 g, 6.11 mmol) was gradually dropped in the resultant reaction solution at room temperature. After completion of the dropping, the reaction solution was agitated at room temperature for 16 hours.

60 ml of iced water was gradually added to the resultant reaction solution to separate an organic layer therefrom. The aqueous layer was extracted three times with chloroform, and the resultant organic layer was mixed with the previously separated organic layer. 60 g of manganese dioxide (chemically treated product) was added to the thus mixed organic layer and agitated for 30 minutes, after which 100 g of sodium sulfate was further added, followed by agitation for 30 minutes.

The resulting mixed solution was filtered and concentrated, and the residue was purified through column chromatography (silica gel, developing solvent: n-hexane/chloroform = 8:1 \rightarrow 4:1), followed by recrystallization (solvent for recrystallization: chloroform/n-hexane = 2:1) to obtain the intended compound (0.72 g, yield: 35.4%).

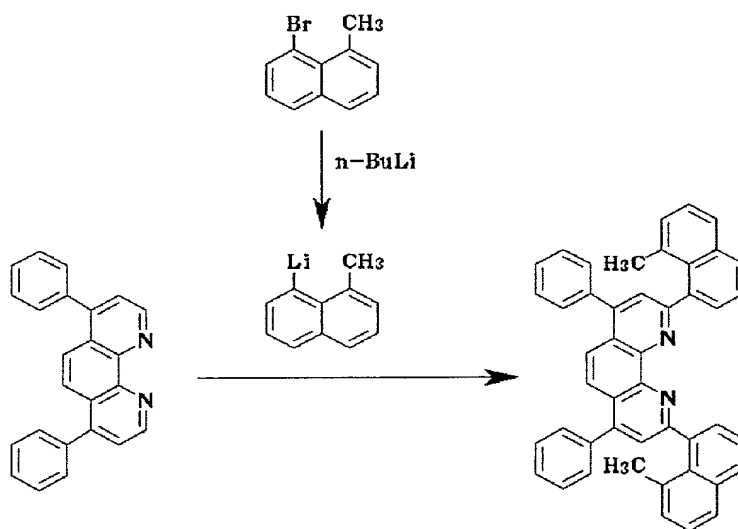
The product was identified through ^1H -NMR and FAB-MS measurements.

¹H-NMR: 2.35 (m, 6H, CH₃-Ar-), 4.65 (m, 4H, CH₂-Ar-),
7.25 - 7.78 (s, 20H, aromatic), 7.81 (s, 2H, aromatic)
MS: m/s (relative intensity) 540 (M⁺, 100)

Example 9

<Preparation of 2,9-di(8-methylnaphthyl)-
bathophenanthroline>

The reaction sequence is shown below



n-Butyl lithium (1.6 M n-hexane solution, 15.3 ml, 24.4 mmol) was gradually dropped, at 0°C, in an n-hexane/anhydrous diethyl ether (1:1) solution (60 ml) of 1-bromo-8-methylnaphthalene (5.34 g, 24.4 mmol). After completion of the dropping, the reaction solution was agitated at room temperature for 16 hours, and the

002011 8940260

resultant product was subsequently separated by filtration, and the residue was washed with n-hexane (40 ml × 3 times). A toluene solution (80 ml) of bathophenanthroline (2.03 g, 6.11 mmol) was gradually dropped, at room temperature, in an anhydrous diethyl ether solution (40 ml) of the resulting solids. After completion of the dropping, the reaction solution was agitated at room temperature for 16 hours.

60 ml of iced water was gradually added to the resultant reaction solution to separate an organic layer therefrom. The aqueous layer was extracted three times with chloroform, and the resultant organic layer was mixed with the previously separated organic layer. 60 g of manganese dioxide (chemically treated product) was added to the thus mixed organic layer and agitated for 30 minutes, after which 100 g of sodium sulfate was further added, followed by agitation for 30 minutes.

The resulting mixed solution was filtered and concentrated, and the residue was purified through column chromatography (silica gel, developing solvent: n-hexane/chloroform = 8:1 → 4:1), followed by recrystallization (solvent for recrystallization: chloroform/n-hexane = 2:1) to obtain the intended compound (1.30 g, yield: 64.0%).

The product was identified through ^1H -NMR and FAB-MS measurements.

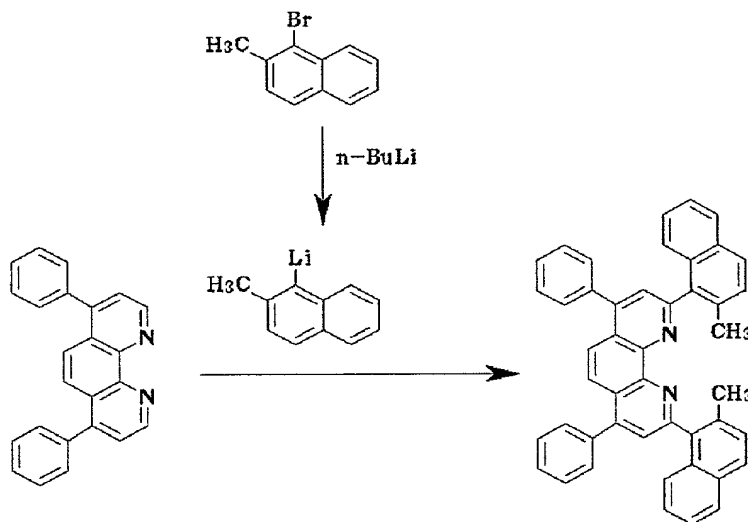
^1H -NMR: 2.60 (m, 6H, $\text{CH}_3\text{-Ar-}$), 7.30 - 7.81 (s, 22H, aromatic), 7.81 (s, 2H, aromatic), 8.25 (s, 2H, aromatic)

MS: m/s (relative intensity) 612 (M^+ , 100)

Example 10

<Preparation of 2,9-di(2-methylnaphthyl)-
bathophenanthroline>

The reaction sequence is shown below



n -Butyl lithium (1.6 M n -hexane solution, 15.3 ml, 24.4 mmol) was gradually dropped, at 0°C , in an n -hexane/anhydrous diethyl ether (1:1) solution (60 ml) of 1-bromo-2-methylnaphthalene (5.34 g, 24.4 mmol). After

00201189540750

completion of the dropping, the reaction solution was agitated at room temperature for 16 hours, and the resultant product was subsequently separated by filtration, and the residue was washed with n-hexane (40 ml × 3 times). A toluene solution (80 ml) of bathophenanthroline (2.03 g, 6.11 mmol) was gradually dropped, at room temperature, in an anhydrous diethyl ether solution (40 ml) of the resulting solids. After completion of the dropping, the reaction solution was agitated at room temperature for 16 hours.

60 ml of iced water was gradually added to the resultant reaction solution to separate an organic layer therefrom. The aqueous layer was extracted three times with chloroform, and the resultant organic layer was mixed with the previously separated organic layer. 60 g of manganese dioxide (chemically treated product) was added to the thus mixed organic layer and agitated for 30 minutes, after which 100 g of sodium sulfate was further added, followed by agitation for 30 minutes.

The resulting mixed solution was filtered and concentrated, and the residue was purified through column chromatography (silica gel, developing solvent: n-hexane/chloroform = 8:1 → 4:1), followed by recrystallization (solvent for recrystallization:

chloroform/n-hexane = 2:1) to obtain the intended compound (1.20 g, yield: 59.1%).

The product was identified through ^1H -NMR and FAB-MS measurements.

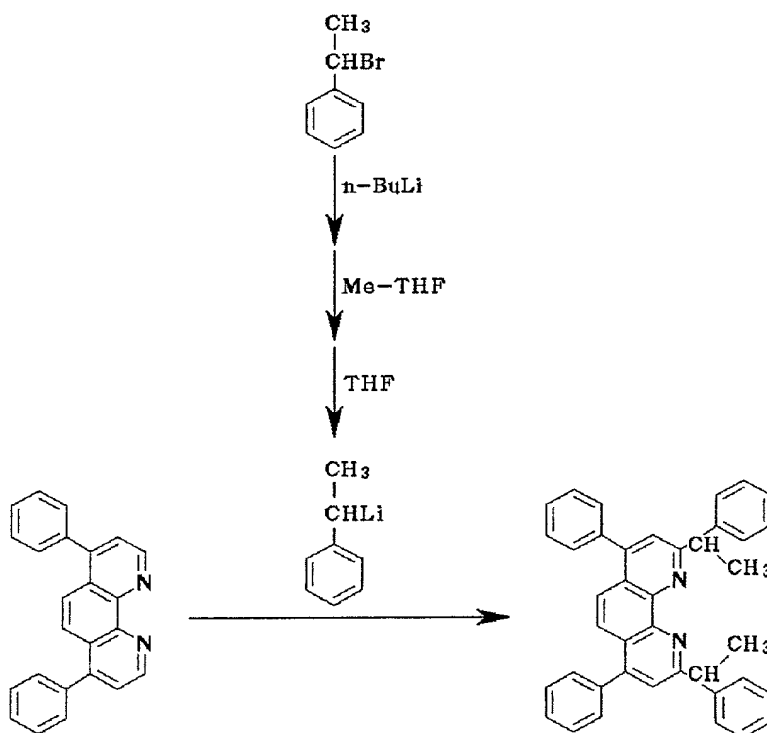
^1H -NMR: 2.80 (m, 6H, $\text{CH}_3\text{-Ar-}$), 7.25 - 7.78 (s, 24H, aromatic), 7.81 (s, 2H, aromatic)

MS: m/s (relative intensity) 612 (M^+ , 100)

Example 11

<Preparation of 2,9-di(α -methylbenzyl)-bathophenanthroline>

The reaction sequence is shown below



00201 8940260

n-Butyl lithium (1.6 M n-hexane solution, 4.45 ml, 7.13 mmol) was gradually dropped in 1-bromo-1-phenylethane (4.91 g, 24.9 mmol) at room temperature. After completion of the dropping, Me-THF (0.627 g, 7.47 mmol) was added in 20 minutes at -22°C, after which THF (1.06 g, 14.7 mmol) was further added in 30 minutes, followed by further agitation at 6 to 10°C for 16 hours. A toluene solution (40 ml) of bathophenanthroline (2.03 g, 6.11 mmol) was gradually dropped in the resultant reaction solution at room temperature. After completion of the dropping, the reaction solution was agitated at room temperature for 16 hours.

60 ml of iced water was gradually added to the resultant reaction solution to separate an organic layer therefrom. The aqueous layer was extracted three times with chloroform, and the resultant organic layer was mixed with the previously separated organic layer. 60 g of manganese dioxide (chemically treated product) was added to the thus mixed organic layer and agitated for 30 minutes, after which 100 g of sodium sulfate was further added, followed by agitation for 30 minutes.

The resulting mixed solution was filtered and concentrated, and the residue was purified through column chromatography (silica gel, developing solvent: n-

hexane/chloroform = 8:1 \rightarrow 4:1), followed by recrystallization (solvent for recrystallization: chloroform/n-hexane = 2:1) to obtain the intended compound (0.83 g, yield: 40.9%).

The product was identified through ^1H -NMR and FAB-MS measurements.

^1H -NMR: 2.40 (m, 6H, $\text{CH}_3\text{-Ar-}$), 4.64 (m, 2H, -CH-Ar-), 7.25 - 7.78 (s, 22H, aromatic), 7.81 (s, 2H, aromatic)

MS: m/s (relative intensity) 540 (M^+ , 100)

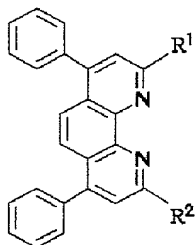
As will be appreciated from the foregoing, the bathophenanthroline compounds of the invention can control, for example, carrier transportability depending on the type of substituent to be introduced into the molecule, thus permitting one to utilize them as a carrier transport material of various types of organic EL devices. Moreover, these compounds have high glass transition point and melting point and are thus stable electrically, thermally and/or chemically. In addition, the compounds are sublimable in nature, thus leading to the advantage that they are readily formed as a uniform amorphous film according to a vacuum deposition process. The bathophenanthroline compound of the invention can be efficiently prepared through nucleophilic substitution reaction using an organolithium

compound.

WHAT IS CLAIMED IS:

1. A bathophenanthroline compound of the following general formula [I]

General Formula [I]:



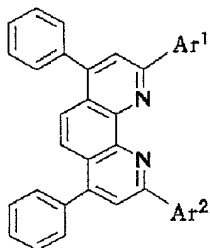
wherein R¹ and R² may be the same or different and independently represent a linear, branched or cyclic, saturated or unsaturated hydrocarbon group, or a substituted or unsubstituted, saturated or unsaturated hydrocarbon group provided that at least one of R¹ and R² has at least two carbon atoms.

2. A bathophenanthroline compound according to Claim 1, wherein said compound is used as an organic layer of an organic electroluminescent device.

3. A bathophenanthroline compound according to Claim 2, wherein said organic layer consists of a carrier transport layer.

4. A bathophenanthroline compound of the following general formula [II]

General Formula [II]:



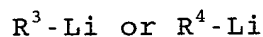
wherein Ar¹ and Ar² may be the same or different and independently represent a substituted or unsubstituted aryl group.

5. A bathophenanthroline compound according to Claim 4, wherein said compound is used as an organic layer of an organic electroluminescent device.

6. A bathophenanthroline compound according to Claim 5, wherein said organic layer consists of a carrier transport layer.

7. A process for preparing a bathophenanthroline compound, which comprising subjecting a lithium compound of the following general formula [III]

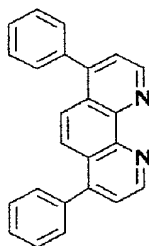
General Formula [III]:



wherein R³ and R⁴ may be the same or different and independently represent a linear, branched or cyclic, saturated or unsaturated hydrocarbon group or a

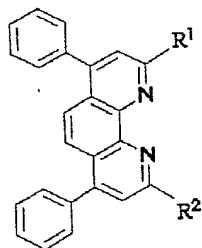
substituted or unsubstituted, saturated or unsaturated hydrocarbon group provided that at least one of R^3 and R^4 has at least two carbon atoms, and bathophenanthroline of the structural formula [IV]

Structural Formula [IV]:



to nucleophilic substitution reaction to obtain a bathophenanthroline compound of the general formula [I]

General Formula [I]:



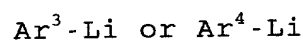
wherein R^1 and R^2 may be the same or different and independently represent a linear, branched or cyclic, saturated or unsaturated hydrocarbon group, or a substituted or unsubstituted, saturated or unsaturated

hydrocarbon group provided that at least one of R¹ and R² has at least two carbon atoms.

8. A process according to Claim 7, wherein said nucleophilic substitution reaction is carried out in such a way that a carbanion is generated from said lithium compound in a solution and reacted with said bathophenanthroline.

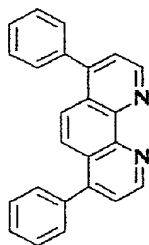
9. A process for preparing a bathophenanthroline compound, which comprising subjecting a lithium compound of the following general formula [V]

General Formula [V]:



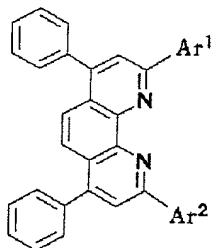
wherein Ar³ and Ar⁴ may be the same or different and independently represent a substituted or unsubstituted aryl group, and bathophenanthroline of the following structural formula [IV]

Structural Formula [IV]:



to nucleophilic substitution reaction to obtain a bathophenanthroline compound of the general formula [III]

General Formula [II]:



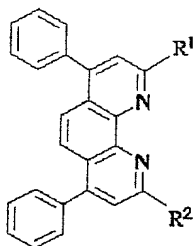
wherein Ar¹ and Ar² may be the same or different and independently represent a substituted or unsubstituted aryl group.

10. A process according to Claim 9, wherein said nucleophilic substitution reaction is carried out in such a way that a carbanion is generated from said lithium compound in a solution and reacted with said bathophenanthroline.

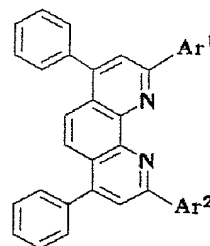
ABSTRACT OF THE DISCLOSURE

A novel bathophenanthroline compound of the general formula [I] or [II] is provided

General Formula [I]:



General Formula [II]:



wherein R¹ and R² may be the same or different and independently represent a linear, branched or cyclic, saturated or unsaturated hydrocarbon group, or a substituted or unsubstituted, saturated or unsaturated hydrocarbon group provided that at least one of R¹ and R² has at least two carbon atoms, and wherein Ar¹ and Ar² may be the same or different and independently represent a substituted or unsubstituted aryl group. A process for preparing the compound is also provided wherein bathophenanthroline and an organolithium compound are subjected to nucleophilic substitution reaction to obtain the compound of the above formula [I] or [II].

FIG. 1

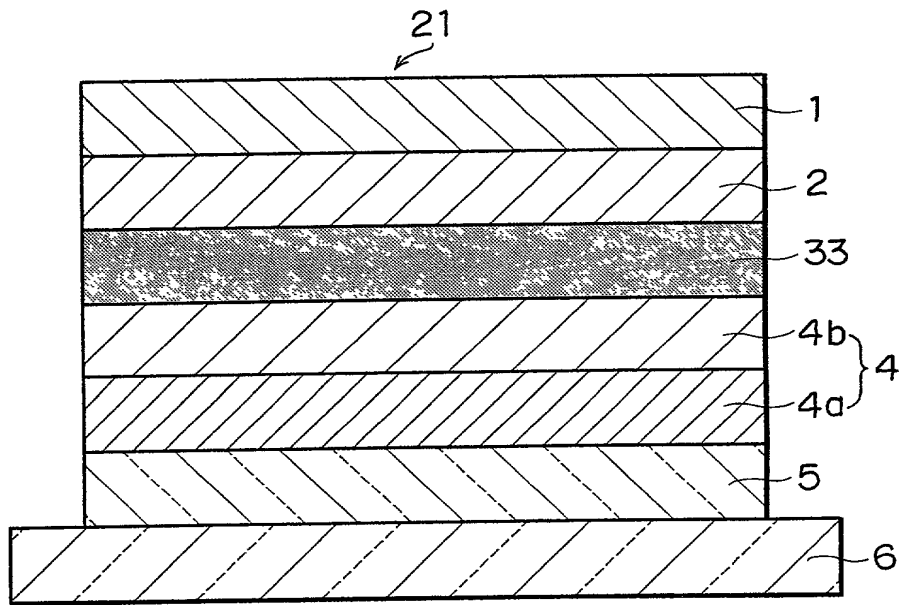


FIG. 2

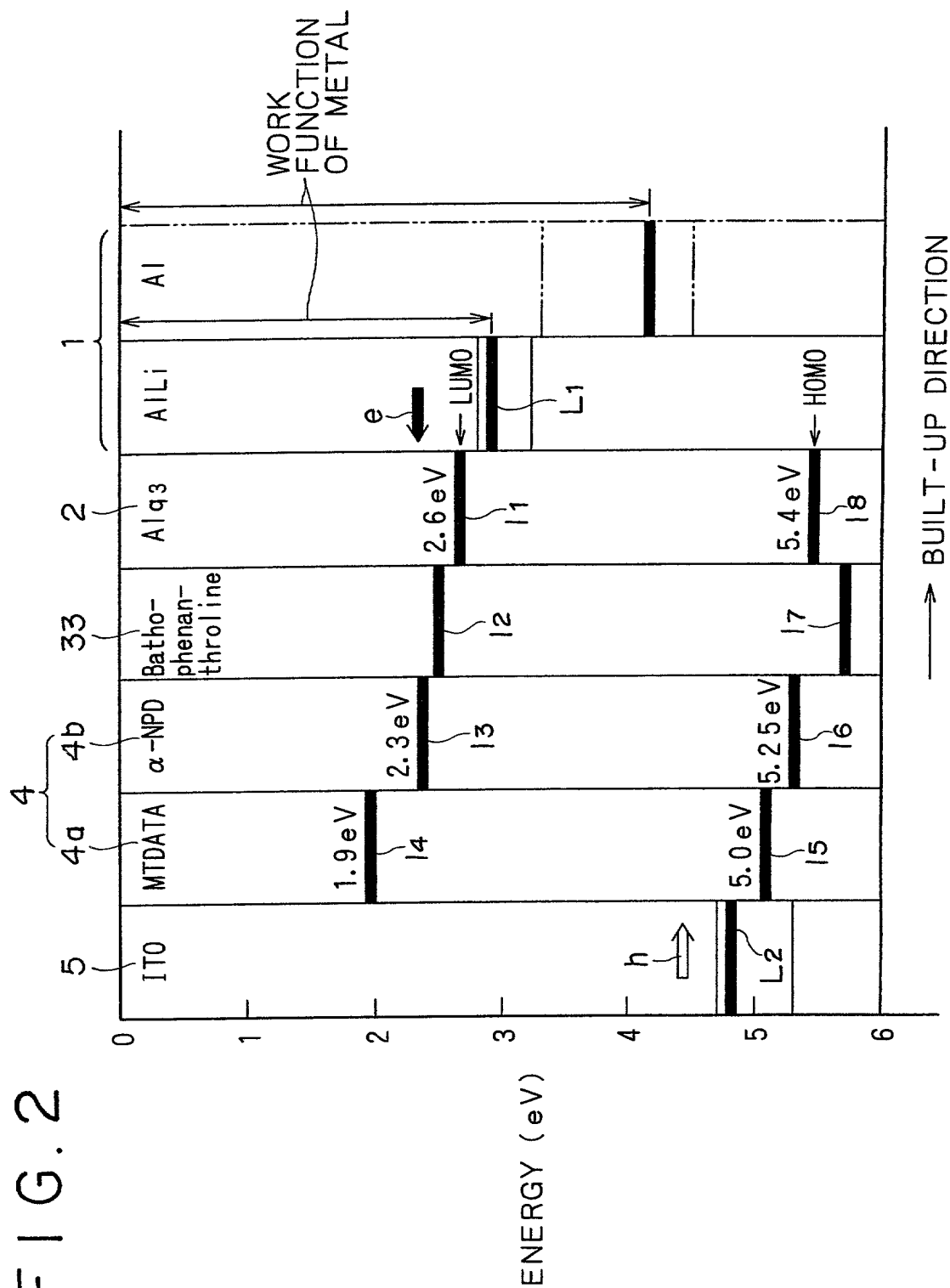
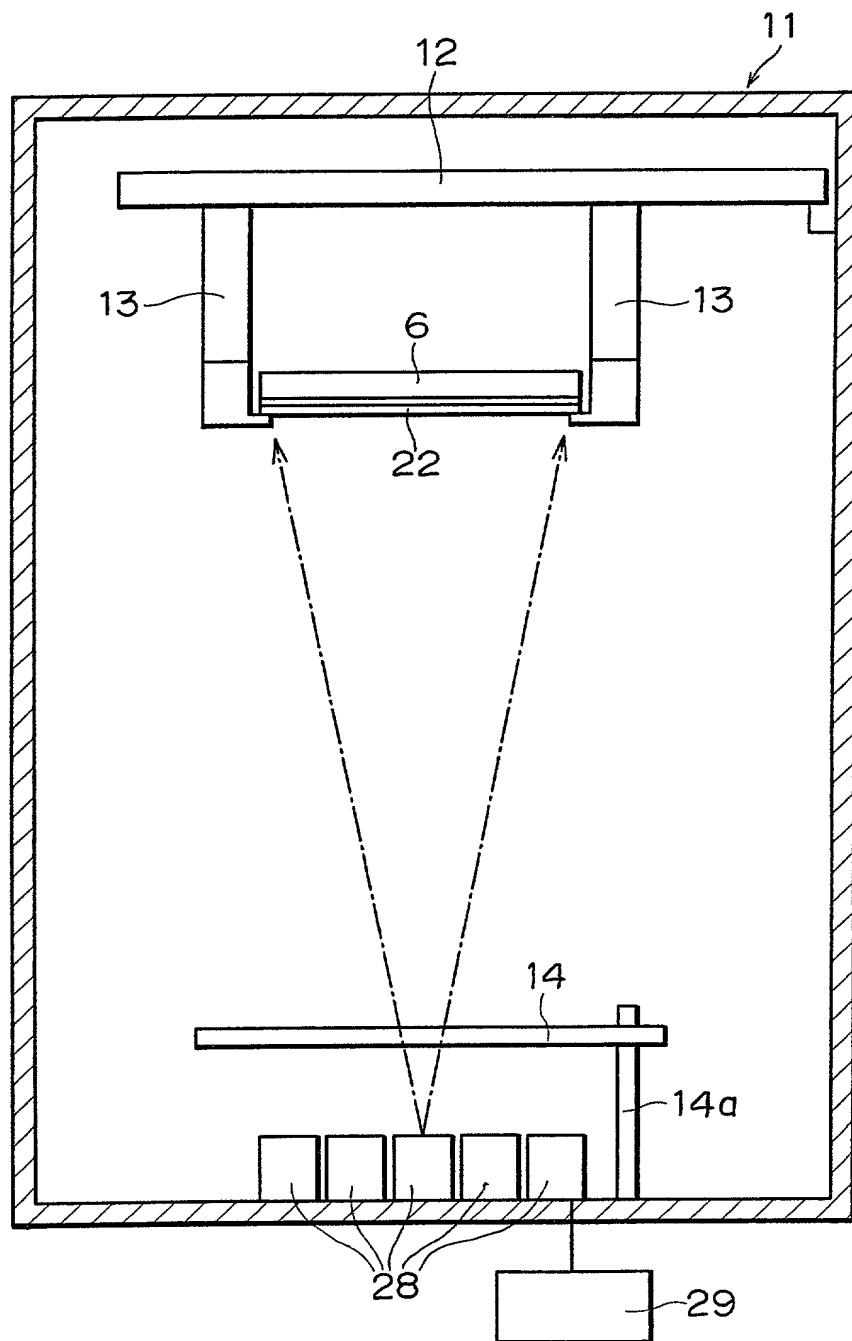


FIG. 3



00207 25640/60

FIG. 4

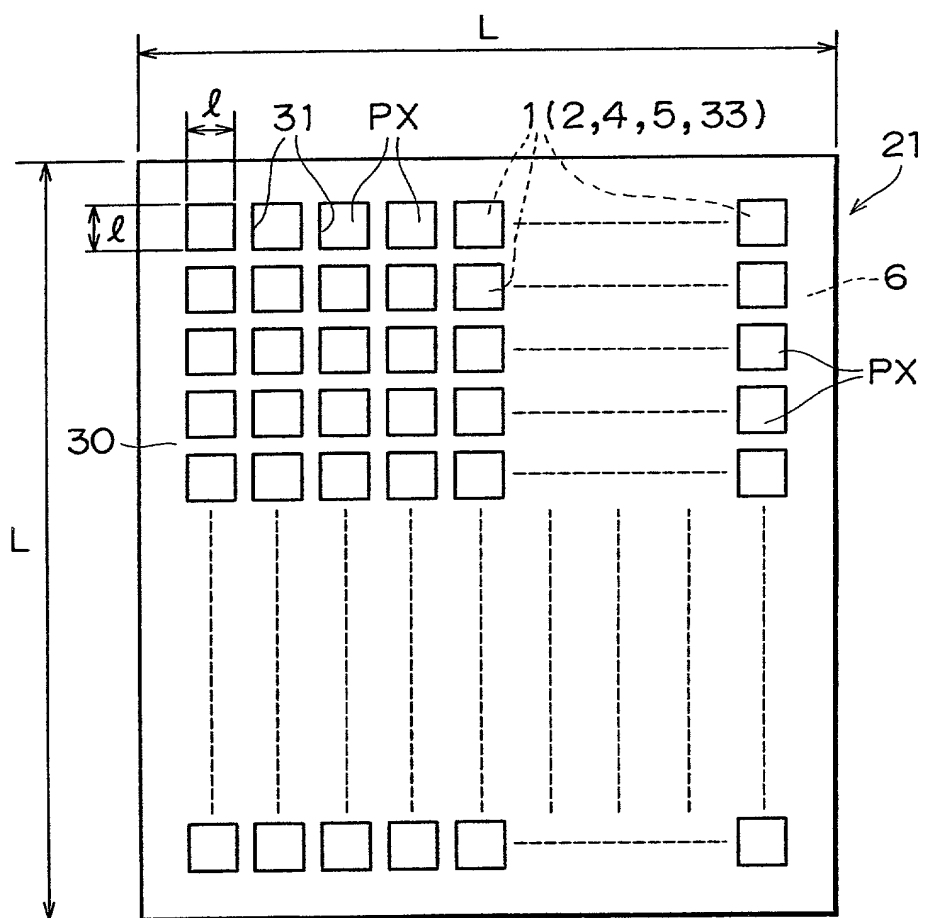


FIG. 5

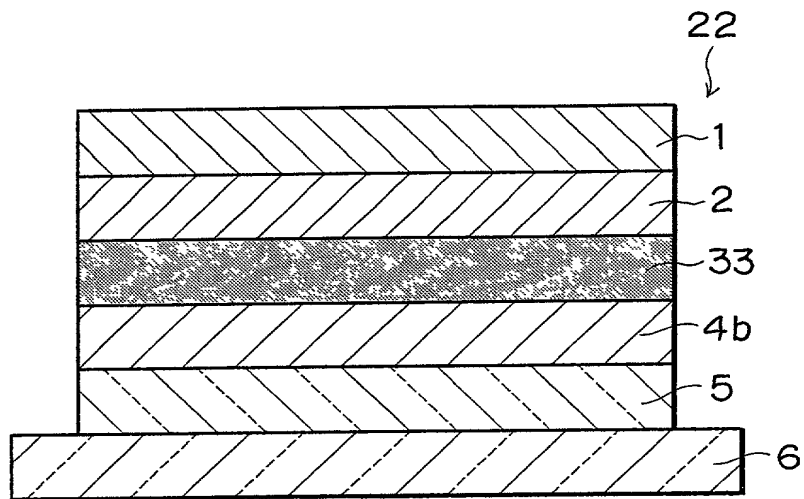


FIG. 6

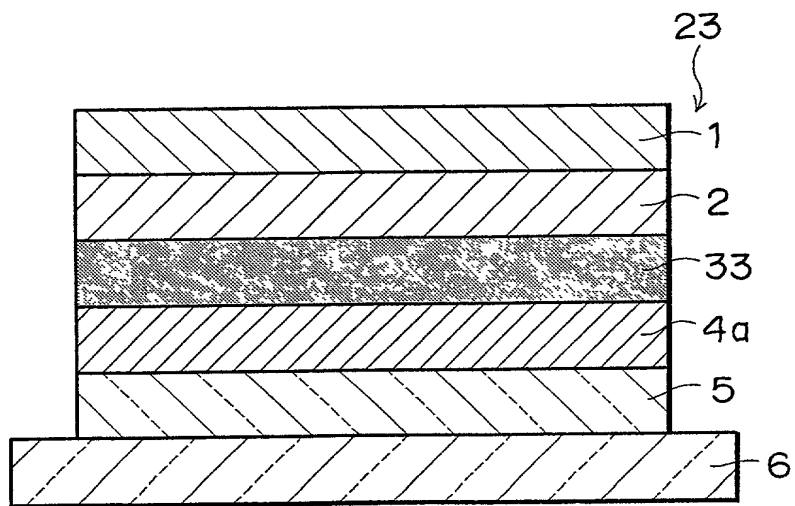


FIG. 7

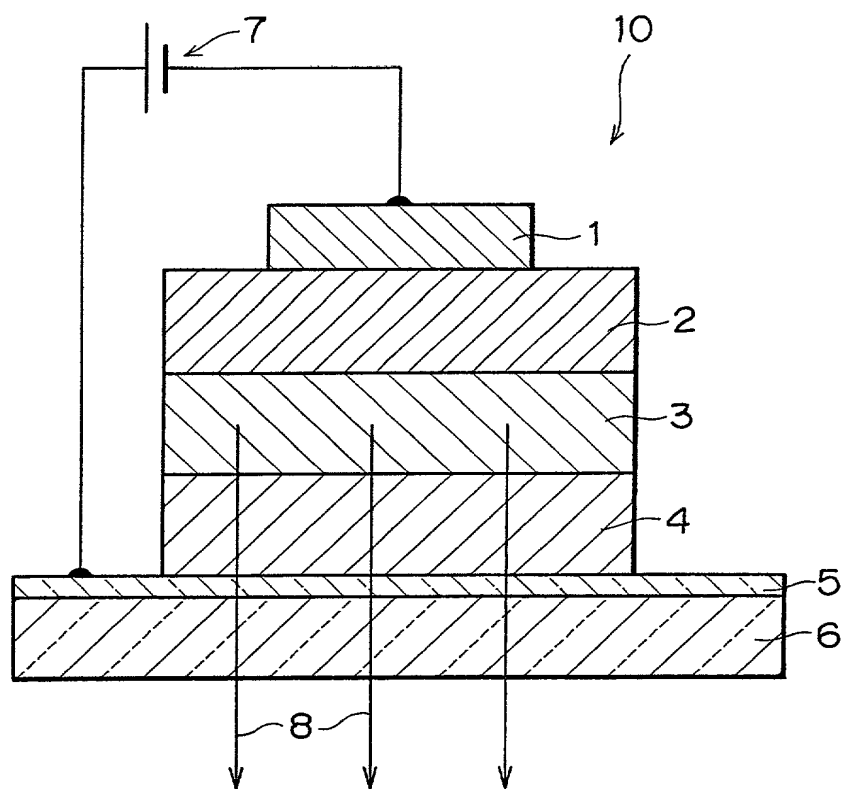


FIG. 8

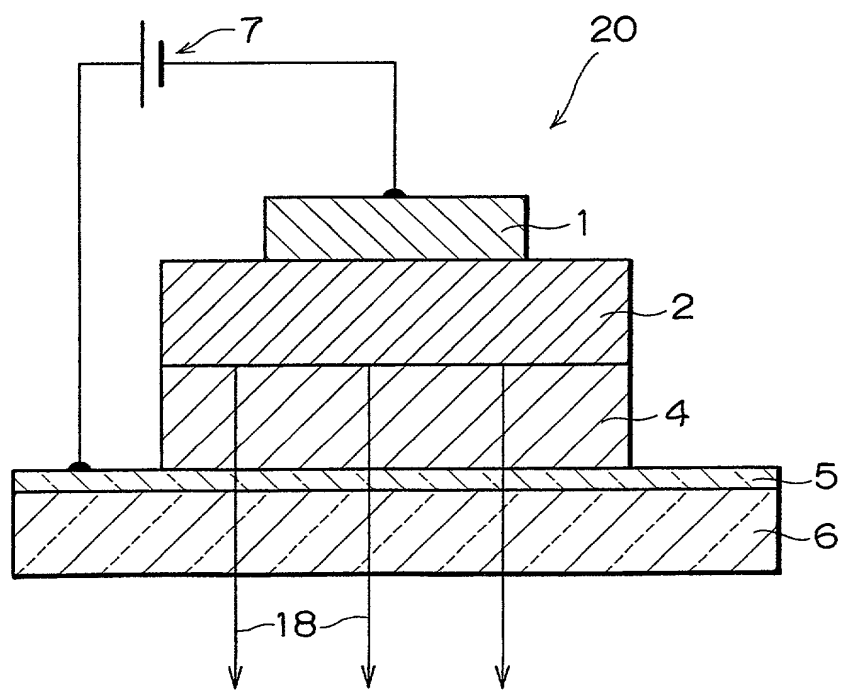
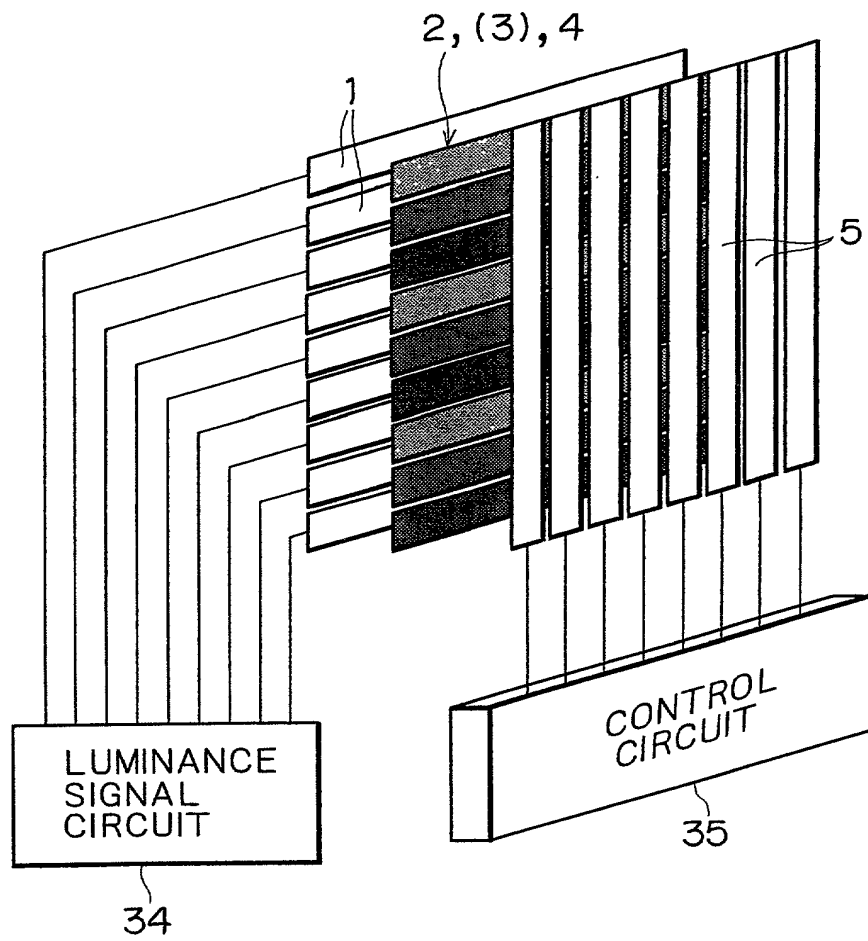


FIG. 9



DECLARATION AND POWER OF ATTORNEY FOR PATENT APPLICATION

特許出願宣言書及び委任状

Japanese Language Declaration

日本語宣言書

下記の氏名の発明者として、私は以下の通り宣言します。

私の住所、私書箱、国籍は下記の私の氏名の後に記載された通りです。

下記の名称の発明に関して請求範囲に記載され、特許出願している発明内容について、私が最初かつ唯一の発明者（下記の氏名が一つの場合）もしくは最初かつ共同発明者であると（下記の名称が複数の場合）信じています。

上記発明の明細書（下記の欄でx印がついていない場合は、本書に添付）は、

☐ __月__日に提出され、米国出願番号または特許協定条約国際出願番号を____とし、
（該当する場合）____に訂正されました。

私は、特許請求範囲を含む上記訂正後の明細書を検討し、内容を理解していることをここに表明します。

私は、連邦規則法典第37編第1条56項に定義されたとおり、特許資格の有無について重要な情報を開示する義務があることを認めます。

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

"BATHOPHENATHROLINE COMPOUND AND PROCESS FOR PREPARING THE SAME"

the specification of which is attached hereto unless the following box is checked:

☐ was filed on _____ as United States Application Number or PCT International Application Number _____ and was amended on _____ (if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56.

(Application No.)
[出願番号]

(Filing Date)
[出願日]

(Status: patented, pending, abandoned)
{現況: 特許許可済, 係属中, 放棄済}

Application No.)
[出願番号]

(Filing Date)
[出願日]

(Status: patented, pending, abandoned)
{現況: 特許許可済, 係属中, 放棄済}

私は、私自身の知識に基づいて本宣誓書中で私が行なう表明が真実であり、かつ私の入手した情報と私の信じることに基づく表明が全て真実であると信じていること、さらに故意になされた虚偽の表明及びそれと同等の行為は米国法典第18編第1001条に基づき、罰金または拘禁、もしくはその両方により処罰されること、そしてそのような故意による虚偽の声明を行なえば、出願した、又は既に許可された特許の有効性が失われることを認識し、よってここに上記のごとく宣誓を致します。

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

委任状: 私は下記の発明者として、本出願に関する一切の手続きを米特許商標局に対して遂行する弁理士または代理人として、下記の者を指名いたします。(弁理士、または代理人の氏名及び登録番号を明記のこと)

POWER OF ATTORNEY: As a named Inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. (list name and registration number)

David R. Metzger (Reg. No. 32,919), Joseph A. Mahoney (Reg. No. 38,956), Howard B. Rockman (Reg. No. 22,190), Jordan A. Sigale, (Reg. No. 39,028), Michael A. Molano (Reg. No. 39,777), Michael L. Kiklis (Reg. No. 38,939), Janelle D. Strode (Reg. No. 34,738), Kevin W. Guynn (Reg. No. 29,972), Jennifer Hammond (Reg. No. 41,814), Lana Knedlik (Reg. No. 42,748), John F. Griffith (Reg. No. 44,137), Marina Saito (Reg. No. 42,121), Alison P. Schwartz (Reg. No. 43,863), Christopher P. Rauch (Reg. No. 45,034), Francisco Rubio-Campos (Reg. No. 45,358), Brian J. Gill (Reg. No. 46,727) and Shashank S. Upadbye, all members of the firm of Sonnenschein, Nath & Rosenthal

Send Correspondence to:

書類送付先

David R. Metzger
Sonnenschein Nath & Rosenthal
P.O. Box #061080
Wacker Drive Station
Chicago, Illinois 60606-1080

直接電話連絡先: (名前及び電話番号)

Direct Telephone Calls to: (name and telephone number)

312/876-2578

Japanese Language Declaration

(日本語宣言書)

唯一または第一発明者名	Full name of sole or first inventor: TETSUO SHIBANUMA
発明者の署名 日付	Inventor's signature Date
住所	Residence Kanagawa, Japan
国籍	Citizenship Japan
私書箱	Post Office Address c/o Sony Corporation 7-35, Kitashinagawa 6-chome
	Shinagawa-ku, Tokyo 141, Japan

(第三以降の共同発明者についても同様に記載し、署名をすること)

第二共同発明者	Full name of second joint inventor, if any: YASUNORI KIJIMA
発明者の署名 日付	Inventor's signature Date
住所	Residence Tokyo, Japan
国籍	Citizenship Japan
私書箱	Post Office Address c/o Sony Corporation 7-35, Kitashinagawa 6-chome
第二共同発明者	Full name of third joint inventor, if any: NOBUTOSHI ASAI
発明者の署名 日付	Inventor's signature Date
住所	Residence Kanagawa, Japan
国籍	Citizenship Japan
私書箱	Post Office Address c/o Sony Corporation 7-35, Kitashinagawa 6-chome
	Shinagawa-ku, Tokyo 141, Japan

Japanese Language Declaration

(日本語宣言書)

第二共同発明者	Full name of fourth joint inventor, if any: SHINICHIRO TAMURA
発明者の署名 日付	Inventor's signature Date
住所	Residence Kanagawa, Japan
国籍	Citizenship Japan
私書箱	Post Office c/o Sony Corporation 7-35, Kitashinagawa 6-chome
	Shinagawa-ku, Tokyo 141, Japan
第二共同発明者	Full name of fifth joint inventor, if any:
発明者の署名 日付	Inventor's signature Date
住所	Residence
国籍	Citizenship
私書箱	Post Office Address
第二共同発明者	Full name of sixth joint inventor, if any:
発明者の署名 日付	Inventor's signature Date
住所	Residence
国籍	Citizenship
私書箱	Post Office Address
第二共同発明者	Full name of seventh joint inventor, if any:
発明者の署名 日付	Inventor's signature Date
住所	Residence
国籍	Citizenship
私書箱	Post Office Address